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AN ANALYSIS OF SOME OF THE PHYSICAL  
AND CHEMICAL PROPERTIES OF SILICA ( $\text{SiO}_2$ )  
OF IMPORTANCE IN ABLATION BEHAVIOR

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AN ANALYSIS OF SOME OF THE PHYSICAL AND  
CHEMICAL PROPERTIES OF SILICA ( $\text{SiO}_2$ )  
OF IMPORTANCE IN ABLATION BEHAVIOR

by

Harold L. Schick

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27 October 1958  
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APPROVED



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RESEARCH AND ADVANCED DEVELOPMENT DIVISION  
AVCO MANUFACTURING CORPORATION  
WILMINGTON, MASSACHUSETTS

## ABSTRACT

The physical properties and thermochemistry of decomposition of  $\text{SiO}_2$  at high temperatures has been thoroughly reviewed and detailed calculations have been made of thermodynamic properties of interest for re-entry vehicle applications. Available thermodynamic data indicate that the primary reaction involved in the vaporization of  $\text{SiO}_2$  under neutral conditions is



The vapor pressure relation corresponding to this equilibrium is

$$P_t = \frac{3}{2} e^{18.41 \left(1 - \frac{3160}{T}\right)} \quad (2)$$

where  $p_t$  is total vapor pressure in atmosphere. A normal boiling point of  $3085^\circ\text{K}$  is predicted from this relation. If other equilibria are considered, including formation of  $\text{SiO}_{2(g)}$ , dimer formation, and dissociation of oxygen, a more refined boiling point of  $3070^\circ \pm 70^\circ \text{K}$  ( $2800^\circ \text{C}$ ) is obtained. This value has been compared with data in the literature and is consistent with the most reliable data available. When  $\text{SiO}_2$  is heated from room temperature to its boiling point and decomposed at that temperature, the total heat absorption is calculated to be 6650 Btu/lb.

Many other physical properties of  $\text{SiO}_2$  which are of interest for re-entry vehicle design purposes, have been reviewed and are summarized in an appendix at the end of the report.

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## I. INTRODUCTION

One of the most promising inorganic compounds for potential use as a consumable material on ablating nose cones is fused silica.<sup>1</sup> To predict the behavior of this material when subjected to the high heating rates of re-entry, it is necessary to know much about its thermochemistry of decomposition at high temperatures. Once the vapor pressure of silica under equilibrium conditions is known, then it may be possible to predict its vaporization behavior under the nonequilibrium conditions of re-entry. This report presents an extensive analysis of the thermochemistry of silica. Other properties such as viscosity of the melt, thermal shock resistance, etc. are also of interest and have been included.

Although the glass industry is an old one and  $\text{SiO}_2$  is one of the most plentiful compounds on the earth's crust, there exists a paucity of accurate vapor pressure data for pure  $\text{SiO}_2$  at elevated temperatures. The data of Brewer and Mastick,<sup>2</sup> and Porter, Chupka, and Inghram<sup>3</sup> represent the most recent available data on the vapor pressure of  $\text{SiO}_2$ . Their data were all obtained below 2,000° K but in this memorandum they are shown to agree satisfactorily with vapor pressures calculated from other available thermodynamic data. The tabulated boiling points for  $\text{SiO}_2$ , which are recorded in various handbooks, have values of 2,230° C, 2,590° C and 2,950° C. These have all been traced to the work of Ruff and co-authors.<sup>4,5,6</sup> All of the boiling point determinations can be criticized because they were carried out in a reducing atmosphere. Since a reducing atmosphere leads to a higher vapor pressure than would be expected, the lower boiling points are not considered to represent the properties of the material. Moreover, the two higher boiling points, 2,590° C and 2,950° C, have been based on a single vapor pressure determination -- 11 mm at 2,060° C. In their original paper, Ruff et al<sup>5</sup> stated that this measurement yields 2,590° C as a boiling point. Some nine years later Ruff<sup>7</sup> stated without further evidence that this was in error and should be 2,950° C. A review of Ruff's extrapolation has indicated that he was probably correct the first time in evaluating his data to obtain a normal boiling point of 2,590° C. However, the original criticism that his measurement was done under reducing conditions is still valid, and the actual boiling point is probably above 2,590° C as he himself stated in his original paper.<sup>5</sup>

In the present paper various possible reactions, which can occur when  $\text{SiO}_2$  vaporizes, have been considered. From available thermochemical data the free energy change for each reaction has been obtained as a function of temperature. Hence, equilibrium constants for these reactions can also be given as functions of temperature. It is then possible to estimate the various species or products present at equilibrium at different temperatures and pressures.

## II. THERMOCHEMISTRY OF THE REACTION $\text{SiO}_{2(l)} \rightarrow \text{SiO}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$ .

The above reaction has been considered by Brewer et al<sup>8, 2</sup> and Porter et al<sup>3</sup> to be the most important one occurring when  $\text{SiO}_2$  decomposes under neutral conditions. The results of the present study are consistent with these earlier findings. Under oxidizing conditions (i. e., with excess oxygen present), the above reaction can be shifted to the left so that  $\text{SiO}_2$  gas formation is repressed.

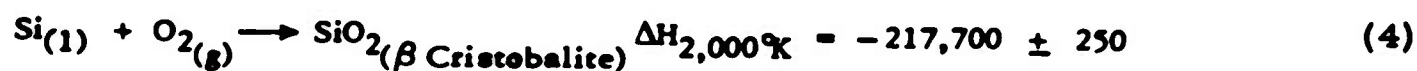
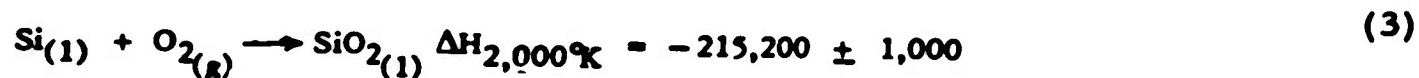
The equilibrium constant of the reaction and the equilibrium vapor pressure of liquid  $\text{SiO}_2$  can be obtained by calculation from the heat of reaction and entropy change of the reaction. First we calculate the heat of reaction and entropy change for the reaction from available data.

### A. HEAT OF REACTION

To calculate the heat of the above reaction we can subtract the heat of formation of  $\text{SiO}_{2(l)}$  from the heat of formation of the products. Since the heat of formation of the elements is taken to be zero, it is necessary to evaluate the heat of formation of  $\text{SiO}_{2(l)}$  and  $\text{SiO}_{(g)}$  only. For the present case, the temperature range from 2,000 to 3,000° K has been considered of primary interest. Because data for this temperature range are not available, it is necessary to use existing data for lower temperatures and calculate the thermodynamic functions at the higher temperatures by extrapolation.

#### 1. Heat of Formation of $\text{SiO}_{2(l)}$

Coughlin<sup>9</sup> has tabulated values for the heat and free energy of formation of  $\text{SiO}_2$  up to 2,000° K. His results are based on the heat of formation data of Humphrey and King.<sup>10</sup> His heat of formation data at 2,000° K are



$\beta$ -cristobalite has a melting point of 1,723° C (1,996° K), according to Levin et al,<sup>12</sup> and a value of 1,728° C (2,001° K), according to Campbell<sup>11</sup> For convenience, we can take 2,000° K as the melting point of cristobalite with negligible error. The diagrams of Levin et al<sup>12</sup>

indicate that silica glass is the stable condensed species of  $\text{SiO}_2$  above  $2,000^\circ \text{K}$ . In further discussions, the terms silica glass or silica liquid are used interchangeably for the range above  $2,000^\circ \text{K}$ .

In any thermochemical calculation, it is desirable to start with the most accurate data available. Referring to the reactions (3) and (4), it might seem preferable to start with reaction (4) rather than reaction (3) since its heat of formation is given to a greater precision. However, the uncertainty in the heat of fusion of  $\beta$ -cristobalite makes either reaction a suitable starting point. Thus, we take the difference between reactions (4) and (3) as the heat of fusion of  $\beta$ -cristobalite,  $\Delta H_f = 2500$  calories/mole. From the entropy data of Kelley<sup>13, 14</sup> we calculate a heat of fusion at  $2,000^\circ \text{K}$  of 2,060 calories/mole. A value of 3,600 calories/mole is quoted by Kubaschewski and Evans<sup>15</sup>. The NBS compilation<sup>16</sup> gives a value of 1,840 calories/mole. The original data quoted by Kelley<sup>17</sup> indicates experimental values for the heat of fusion of cristobalite to be in the range of 1,000 to 3,700 calories/mole. He derives 2,100 calories/mole as an average value. This range in values for the heat of fusion shows why the data for reaction (3) are less precise, but still the best available. Therefore, the data for reaction (3) are used for the present calculations.

The heat of formation at temperatures above  $2,000^\circ \text{K}$  can be calculated by means of the Kirchoff relation:

$$\Delta H_T = \Delta H_{2000} + \int_{2000}^T \Delta C_p dT$$

or

$$\Delta H_T = \Delta H_{2000} + (H_T - H_{2000})_{\text{SiO}_{2(l)}} - (H_T - H_{2000})_{\text{Si}_{(l)}} - (H_T - H_{2000})_{\text{O}_2} \quad (5)$$

The results of such a calculation at  $2,000^\circ$ ,  $2,500^\circ$ , and  $3,000^\circ \text{K}$  are given in Table I. For this calculation, the heat content of  $\text{SiO}_{2(l)}$  was estimated by assuming that its average heat capacity was 1 calorie/mole degree greater than that given by Kelley<sup>13</sup> for  $\text{SiO}_{2(\text{glass})}$  at  $2,000^\circ \text{K}$ . That is,  $C_p = 21.66$  was assumed.

According to Kubaschewski and Evans<sup>15</sup>, a rough estimate of the heat capacity of molten liquids can be obtained by assuming that each atom contributes 7.25 calories/g. atom $^\circ \text{K}$ . This leads to a value of 21.75 calorie/mole $^\circ \text{K}$ . In the paper by Humphrey et al<sup>18</sup>, the heat capacity of liquid silica was taken to be  $C_p = 24.0$ . In the present case,

TABLE I  
CALCULATION OF HEAT OF FORMATION OF  $\text{SiO}_2(\text{liq})$

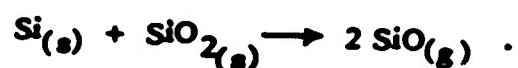
$\text{SiO}_2(\text{g})$	Temperatures in Degrees K					Remarks and Sources of Data
	0	298	2000	2500	3000	
1. $H_T - H_{298}$			$29,010 \pm 580$	$39,840 \pm 1100$	$50,670 \pm 1600$	{ data at $2000^\circ\text{K}$ . from Ref. 13 { data at $2500$ and $2000^\circ\text{K}$ . derived in line 2. From $C_p$ data of line 3. $C_p$ was chosen to have an average value of $21.66$ in range above $2000^\circ\text{K}$ . This is 1 cal/mole-degree over Kelley's value at $2000^\circ\text{K}$ . Uncertainty is estimate.
2. $H_T - H_{2000}$			0	$10,830 \pm 500$	$21,660 \pm 1000$	
3. $C_p$	$C_p = 13.38 + 3.68 \times 10^{-3}T - 3.45 \times 10^{-5}T^{-2}$ for $T = (298 - 2000^\circ\text{K})$ ; 2%		$21.66 \pm 0.43$	$21.66 \pm 1.0$	$21.66 \pm 1.0$	
$\text{Si}_2(\text{l})$						
4. $H_T - H_{2000}$			0	$3500 \pm 70$	$7000 \pm 140$	Ref. 25 (our estimate is 2% for uncertainty).
$\text{O}_2(\text{g})$						
5. $H_T - H_{2000}$			0	$4583 \pm 45$	$9297 \pm 90$	Ref. 25 (our estimate is 1% for uncertainty).
$\text{SiO}_2$						
6. Heat of formation of $\text{SiO}_2(\text{liq})$			$-215,200 \pm 1000$	$-212,453 \pm 1615$	$-210,467 \pm 2230$	Ref. 9 Used Data for liquid phase at $2000^\circ\text{K}$ . For $2500^\circ$ } $\Delta H_T = \Delta H_{2000} + (H_T - H_{2000}) \text{SiO}_2$ and $3000^\circ$ } $-(H_T - H_{2000})\text{Si}_2(\text{l}) - (H_T - H_{2000})\text{O}_2$

the extrapolation to high-temperatures leads to considerable uncertainty in the heat content. The uncertainty in the heat capacity is roughly estimated to be 1 calorie/mole-degree thus giving  $C_{pSiO_{2(l)}} = 21.66 \pm 1.0$ .

Sources of data for the calculations of Table I are given in the table. Rough estimates of the uncertainties in the data have been made. The final values for the heat of formation in the temperature range 2,000 to 3,000° K become more uncertain as temperature rises because of the uncertainty in the heat capacity of liquid  $SiO_2$  in this range.

## 2. Heat of Formation of $SiO(g)$

The heat of formation of  $SiO(g)$  at 298° K is taken to be  $-21,411 \pm 574$  calories. This value is the one recommended by Edwards and Brewer.<sup>8, 19</sup> It is based on a recalculation of the work of Schafer and Hornle<sup>20</sup> who had studied the reaction



Other sources of data considered by Brewer and Edwards,<sup>8</sup> are given below:

<u>Investigators and Equilibrium Studied</u>	<u><math>\Delta H^\circ_{298}</math> (K calorie/mole)</u>
Grube and Speidel <sup>21</sup>	
$H_{2(g)} + SiO_{2(s)} \rightarrow H_{2O(g)} + SiO(g)$	$-15,291 \pm 2,000$
Brewer and Mastick <sup>2</sup>	
$SiO_{2(s)} \rightarrow Si(g) + \frac{1}{2}O_{2(g)}$	$-21,159 \pm 2,000$
Gel'd and Kochnev <sup>22</sup>	
$Si(s) + SiO_{2(s)} \rightarrow 2SiO(g)$	$-18,212 \pm 960$
Schafer and Hornle <sup>20</sup>	
$Si(s) + SiO_{2(s)} \rightarrow 2SiO(g)$	$-21,411 \pm 570$
Tombs and Welch <sup>23</sup>	
$H_{2(g)} + SiO_{2(s)} \rightarrow H_{2O(g)} + SiO(g)$	Low temperature data $-26,004 \pm 2,400$ High temperature data $-21,269 \pm 1,500$



Brewer and Edwards considered each of the above sources very carefully and chose the data of Schafer and Hornle as being the best. It should be pointed out that the arguments they use, based on dissociation energies of  $\text{SiO}_{(g)}$ , were fortuitously correct inasmuch as more recent data shows they used too low a value for the heat of sublimation of silicon (88.9 Kcalorie/mole) and for the dissociation energy of  $\text{SiO}_{(g)}$ , (169 Kcalorie/mole). A more recent value for the heat of sublimation of monatomic silicon is 105 Kcalorie/mole based on mass spectrometer measurements given by Honig<sup>24</sup> and recommended by Stull and Sinke.<sup>25</sup> Searcy<sup>26</sup> gives a value of 112 Kcalorie/mole and Huggins<sup>27</sup> gives 100 Kcalorie/mole for the heat of sublimation. The results of a very recent study of the sublimation of  $\text{SiC}$  by Drowart, deMaria, and Inghram<sup>28</sup> lead to a value of 113 Kcalorie/mole for the heat of sublimation, in good agreement with Searcy's value by the same method.

It should also be mentioned that a very recent paper by Baird and Taylor<sup>29</sup> gives a heat of reaction to form  $\text{SiC}$  from liquid silicon of -19,250 Kcalorie/mole as compared with earlier values of -23,300 Kcalorie/mole. This leads to a heat of sublimation for silicon of 116 or 117 Kcalorie/mole from the results of Searcy and Drowart et al's work.

However, these high values (112 Kcalorie/mole and greater, based on  $\text{SiC}$  dissociation data) should not necessarily be accepted in preference to Honig's value which is based on a direct measurement. A further complication in the measurements based on  $\text{SiC}$  dissociation is indicated by Baird and Taylor's statement that  $\text{SiC}$  becomes unstable relative to liquid silicon and graphite near 2,050° C.

For the dissociation energy of  $\text{SiO}_{(g)}$ , it is found that Barrow and Rowlinson<sup>30</sup> recommend  $185 \pm 6$  Kcalorie/mole. This agrees with Gaydon's value<sup>31</sup> of  $184 \pm 23$  Kcalorie/mole, but is higher than the value given by Herzberg<sup>32</sup> (171 Kcalorie/mole). By calculation from the values of 105 Kcalorie/mole for the sublimation to monatomic silicon,  $117.9/2$  Kcalorie for the dissociation of one-half mole of oxygen from Stull and Sinke<sup>25</sup> and a heat of dissociation of 185 Kcalorie/mole for  $\text{SiO}_{(g)}$ , a value of -21,100 calorie/mole is obtained for the heat of formation of  $\text{SiO}_{(g)}$  at absolute zero. Other possible combinations are shown in Table II-A.

TABLE II-A

POSSIBLE HEATS OF FORMATION OF  $\text{SiO}_{(g)}$   
FROM SPECTROSCOPIC DATA

Heat of formation of  $\text{SiO}_{(g)}$  at  $0^\circ \text{K}$

$$\Delta H^\circ_f = L_{\text{Si}} + \frac{1}{2}D_{\text{O}_2} - D_{\text{SiO}}$$

<u><math>L_{\text{Si}}</math></u>	<u><math>\frac{1}{2}D_{\text{O}_2}</math></u>	<u><math>D_{\text{SiO}}</math></u>	<u><math>\Delta H^\circ_{f(\text{SiO})}</math></u>
88 (ref 19)	58.9 (ref 25)	169 (ref 19)	-22
88 (ref 19)	58.9 (ref 25)	185 (ref 30)	-38.1
100 (ref 27)	58.9 (ref 25)	169 (ref 19)	-10.1
100 (ref 27)	58.9 (ref 25)	185 (ref 30)	-26.1
105 (ref 24)	58.9 (ref 25)	169 (ref 19)	- 5.1
*105 (ref 24)	58.9 (ref 25)	185 (ref 30)	-21.1
112 (ref 26)	58.9 (ref 25)	169 (ref 19)	+ 1.9
112 (ref 26)	58.9 (ref 25)	185 (ref 30)	-14.1

\* Indicates a combination of data which agree with thermochemical data.

The data in this table shows that a wide range of possible values for the heat of formation of  $\text{SiO}$  could be estimated depending on the choice of the heat of sublimation of silicon and the heat of dissociation of  $\text{SiO}$ . In view of these uncertainties it would appear that the thermochemical data reviewed by Brewer and Edwards<sup>8,19</sup> are probably more reliable. Accordingly, we use their value of  $\Delta H^\circ_{\text{O}} = -21,693 \text{ calorie/mole}$  or  $\Delta H^\circ_{298} = -21,411 \pm 574 \text{ calorie/mole}$ .

It should be noted that the data of Table II-A indicates that larger heats of sublimation of silicon require larger heats of dissociation of  $\text{SiO}$  in order to give heat of formation values consistent with the Brewer value chosen above. Thus, if a value of 117 Kcalorie/mole for silicon sublimation were to become accepted, a heat of dissociation for  $\text{SiO}$  of 197 Kcalorie/mole would be required to correspond to a heat of formation for  $\text{SiO}$  of -21.5 Kcalorie/mole. Such a value for the heat of dissociation

would be within the range estimated by Gaydon ( $184 \pm 23$  Kcalorie/mole.) At this time, it therefore appears that thermochemical data are to be preferred to the spectroscopic data, for the heat of formation of  $\text{SiO}_{(g)}$ .

Having now selected our source data for the heat of formation of  $\text{SiO}_{(g)}$  at lower temperatures, it is necessary to extrapolate these data to high temperatures in the range  $2,000^\circ$  to  $3,000^\circ$  K. To make such an extrapolation, it is necessary to obtain heat capacity data for  $\text{SiO}_{(g)}$  in this temperature range.

To obtain thermodynamic data for  $\text{SiO}_{(g)}$ , it was necessary to make calculations with spectroscopic data. The methods followed are similar to those described by Mayer and Mayer.<sup>33</sup> The molecular weight was taken to be 44.09. Other spectroscopic data were taken from Herzberg.<sup>32</sup> No electronic levels other than the singlet ground state were of importance in these calculations. The next highest electronic state has a wave number of  $42,835 \text{ cm}^{-1}$ , corresponding to  $\frac{hc\omega}{kT} = 20.6$  at  $3,000^\circ$  K; and  $e^{-\frac{hc\omega}{kT}}$  makes a very small contribution to the partition function. For the one vibrational frequency possible in this diatomic molecule, the characteristic frequency ( $\omega = \omega_e - 2\omega_e x_e$ ) is  $1,230 \text{ cm}^{-1}$ . For the rotational contributions, the moment of inertia was taken to be  $I = 38.6 \times 10^{-40} \text{ gm cm}^2$ . The symmetry number is one since the atoms of the molecule are dissimilar. Anharmonicity corrections to the entropy were made at the higher temperatures but were still quite small.

The results of these calculations are tabulated in Table II-B. For comparison purposes the results of Brewer and Edwards<sup>8,19</sup> at the lower temperatures have been included and are found to agree with our data. A further approximate check on our data is indicated by the fact that it was found that the heat capacity term due to vibration at  $2,000^\circ$  K was almost fully excited. Moreover, if for the diatomic gas we assume that translation, rotation, and vibration are contributing fully to the heat capacity at constant pressure, we get  $C_p = 9/2R$ . Therefore

$$S_{3,000} - S_{2,000} = \int_{2,000}^{3,000} \frac{C_p dT}{T} \approx 3.62 \text{ e.u.}$$

From our results in Table II-A the entropy increment is 3.63 e.u. Calculations with the enthalpy data also lead to  $H_{3,000} - H_{2,000} = 8,876$  calorie/mole, giving an average  $C_p$  over this temperature range of 8,876 calorie/mole degree. Thus the data appear to be self-consistent.

With the data from Table II-B and additional data for elemental silicon and oxygen from Stull and Sinke<sup>25</sup>, it is now possible to calculate the heat of formation of gaseous SiO in the temperature range of 2,000° - 3,000° K. The results of such a calculation are summarized in Table III.

The calculation was based on the relation

$$\Delta H_T = \Delta H_o + \int_o^T \Delta C_p dt$$

or

$$\Delta H_T = \Delta H_o + (H_T - H_o)_{\text{SiO}(g)} - (H_T - H_o)_{\text{Si}} - \frac{1}{2}(H_T - H_o)_{\text{O}_2(g)}$$

In order to make an estimate of the uncertainty in this calculation, it was necessary to take into account the accuracy of all the data used in making it. Since Stull and Sinke<sup>25</sup> had not stated the accuracy of their data, we made our own estimate of their accuracy as indicated in Table III. In order to make a partial check on our computation of the heat of formation of SiO<sub>(g)</sub>, we have tabulated the data of Coughlin<sup>9</sup> and Humphrey et al<sup>18</sup> in the second row of the table. Their data for 298° K and 2000° K are in good agreement with ours.

### 3. Heat of the Overall Reaction

In the previous sections, the heats of formation of SiO<sub>2(l)</sub> and SiO<sub>(g)</sub> in the range of 2,000° K - 3,000° K were evaluated. Those results can be readily used to calculate the heat of the overall reaction for the vaporization of liquid SiO<sub>2</sub> by means of the relation  $\Delta H_T = \Delta H_f [\text{SiO}(g)] - \Delta H_f [\text{SiO}_2(l)]$ .

In Table IV are summarized the results of such calculations at 2,000° K, 2,500° K, and 3,000° K.

**TABLE II-B**

**THERMODYNAMIC FUNCTIONS FOR  $\text{SiO}_2$  FROM SPECTROSCOPIC DATA**

**ALL UNITS ARE CALORIE/MOLE-DEGREE K**

$\frac{(F_T^\circ - H_o^\circ)}{T}$	298° K	2,000° K	2,500° K	3,000° K
Translation	-32.30	-41.76	-42.86	-43.76
Electronic	0.00	0.00	0.00	0.00
Vibration	0.00	- 1.05	- 1.34	- 1.61
Rotation	-11.27	-15.05	-15.49	-15.85
$\frac{(F_T^\circ - H_o^\circ)}{T}_{\text{net}}$	-43.57	-57.86	-59.69	-61.22
$\frac{(H - H_o^\circ)}{T}$				
Translation	4.965	4.965	4.965	4.965
Electronic	0.000	0.000	0.00	0.00
Vibration	.00	1.23	1.36	1.46
Rotation	1.987	1.987	1.987	1.987
$\frac{(H - H_o^\circ)}{T}_{\text{net}}$	6.955	8.18	8.317	8.412
$s - \frac{(H - H_o^\circ)}{T}_{\text{net}} - \frac{(F_T^\circ - H_o^\circ)}{T}_{\text{net}}$	50.52	66.04	68.01	69.63
Anharmonicity Corrections	0.00	0.00	0.03	0.04
$s_T$ (our calculation)	50.52	66.04	68.04	69.67
$s_T$ (from Brewer and Edwards <sup>8, 19</sup> )	50.53	66.02		

**TABLE III**  
**CALCULATION OF HEAT OF FORMATION OF  $\text{SiO}_2(\text{g})$  FROM ELEMENTS**

		Temperatures in Degrees K					Remarks and Sources of Data
		0	298	3000	2500	3000	
1. Heat of formation of $\text{SiO}_2(\text{g})$ from elements. (Source data as basis for present calculations.)		-21,695 $\pm$ 574	-21,411 $\pm$ 574				Values at 0°K. and 298°K. from Refs. 8 and 19. Based on recalculated data of Ref. 20. They had studied the reaction $\text{Si}(\text{c}) + \text{SiO}_2(\text{c}) \rightarrow 2 \text{SiO}(\text{g})$ . Brewer and Edwards <sup>4,5</sup> preferred these data to that of Brewer and Mastick. <sup>2</sup>
2. Additional comparative data. Heat of formation of $\text{SiO}_2(\text{g})$			-21,800	-36,700			Refs. 9, 18 also based on data of Ref. 20.
3. $\frac{H_T - H_0}{T}$				8.18	8.32	8.41	Taken from Table II-B
4. $(H_T - H_0^*) \text{SiO}_2(\text{g})$				16,400 $\pm$ 150	20,800	25,230 $\pm$ 250	Error estimated to be 1%.
5. $(H_T - H_{298}) \text{Si}(\text{l})$				21,960 $\pm$ 440	25,460	28,960	Stull and Sinke <sup>25</sup> - we estimate 2%.
6. $H_T - H_{298} \text{Si}(\text{l})$			769	22,729 $\pm$ 460	26,299 $\pm$ 520	29,729 $\pm$ 594	Ref. 25 gives $H_{298} - H_0$
7. $(H_T - H_{298}) \text{O}_2(\text{g})$				14,148 $\pm$ 140	18,731 $\pm$ 100	23,445 $\pm$ 230	Ref. 25.
8. $(H_T - H_0^*) \text{O}_2$			2075	16,223	20,806	25,520	Ref. 25 gives $H_{298} - H_0$
9. $1/2 (H_T - H_0^*) \text{O}_2$				8111 $\pm$ 80	10,403 $\pm$ 100	12,760 $\pm$ 125	
10. Final preferred values of heat of formation of $\text{SiO}_2(\text{g})$		-21,695 $\pm$ 574	-21,411 $\pm$ 574	-36,135 $\pm$ 1264	-37,527 $\pm$ 1394	-38,954	$\Delta H_T^* = \Delta H_0^* + (H_T - H_0) \text{SiO}_2(\text{g}) - 1/2 (H_T - H_0) \text{O}_2$ = Row 1 at 0°K + Row 4 - Row 6 - Row 9.

TABLE IV

HEAT OF THE REACTION  $\text{SiO}_2(1) \rightarrow \text{SiO}(g) + 1/2 \text{O}_2(g)$

	<u>2,000° K</u>	<u>2,500° K</u>	<u>3,000° K</u>
$\Delta H_f(\text{SiO}(g))$	$-36,135 \pm 1,264$ or $(\pm 2,764)$	$-37,527 \pm 1,394$ or $(\pm 2,894)$	$-38,954 \pm 1,543$ or $(\pm 3,043)$
$\Delta H_f(\text{SiO}_2(1))$	<u><math>-215,200 \pm 1,000</math></u>	<u><math>-212,453 \pm 1,615</math></u>	<u><math>-210,467 \pm 2,230</math></u>
$\Delta H_{\text{reaction}}$	$179,065 \pm 2,264$ or $(\pm 3,690)$	$174,926 \pm 2,834$ or $(\pm 4,260)$	$171,513 \pm 3,409$ or $(\pm 4,835)$

Note that uncertainties at 2,500° K and 3,000° K are less than would be calculated by simple addition of the component uncertainties. (See Table V.) A second set of estimated uncertainties (indicated in parenthesis) are 1,500 calorie in excess of those not shown in parenthesis. Thus, Coughlin<sup>9</sup> gave an uncertainty of 2,000 calorie for  $\Delta H_f(\text{SiO}_g)$  at 298° K, whereas Brewer and Edwards gave 574 calorie even though they had both evaluated the same original data. To make the best estimate of the uncertainties in the heats of reaction obtained above, the sums involved in deriving the values must be considered in detail. It is shown by the following algebraic manipulations that some of the uncertainties cancel out. The remaining terms actually used in calculating the heat of reaction, can be added without regard to algebraic sign to get the true uncertainty.

For the reaction  $\text{SiO}_2(1) \rightarrow \text{SiO}(g) + 1/2 \text{O}_2(g)$  it follows that

$$\begin{aligned}
 \Delta H_{\text{reaction}} &= \Delta H_{f(\text{O}_2)} + \Delta H_{f(\text{SiO}_g)} - \Delta H_{f(\text{SiO}_2(1))} \\
 &= 0 + \Delta H_{f(\text{SiO}_g)}^\circ + (H_T - H_0)\text{SiO}(g) - (H_T - H_0)\text{Si}(1) - 1/2(H_T - H_0)\text{O}_2(g) \\
 &\quad - \Delta H_{f(\text{SiO}_2(1))}^{(2,000^\circ)} - (H_T - H_{2000})_{\text{SiO}_2} + (H_T - H_{2000})_{\text{Si}(1)} + (H_T - H_{2000})_{\text{O}_2(g)} .
 \end{aligned}$$

or

$$\Delta H_{\text{reaction}} = \Delta H_{\text{of}}^{\circ}(\text{SiO}_{(g)}) - \Delta H_{2000\text{f}}(\text{SiO}_{2(l)}) + (H_T - H_0)_{(\text{SiO}_{(g)})} - (H_T - H_{2000})_{(\text{SiO}_{2(l)})} \\ - (H_{2000} - H_0)_{\text{Si}_{(l)}} + \frac{1}{2}(H_T - H_{2000})_{\text{O}_{2(g)}} - \frac{1}{2}(H_{2000} - H_0)_{\text{O}_{2(g)}} .$$

Table V shows the magnitudes of the uncertainties of the quantities in the latter equation. Their sums were taken as the true uncertainty. At 3,000° K it is seen that about half of the error arises from the thermochemical data for the heats of formation of the reference materials. This may be somewhat optimistic inasmuch as the other determinations of the heat of formation of  $\text{SiO}_{(g)}$  quoted by Brewer and Edwards<sup>8,19</sup> indicate a possible spread of a few thousand calories per mole. Hence, it is possible that the uncertainty in  $\Delta H_{\text{of}}^{\circ} \text{SiO}_{(g)}$  may be larger than the 574

calorie/mole given. If this uncertainty is 2,000 calories/mole, as chosen by Coughlin, then the resultant uncertainty in the overall heat of reaction at 3,000° K is about 5,000 calories/mole. The 2,000 value for the uncertainty of the heat of formation of  $\text{SiO}_{(g)}$  may be more reasonable than the 574 value since other experimenters' values have had a wider spread than 574 calories. The other large uncertainty contributions arise from the estimation of heat capacity data for liquid  $\text{SiO}_2$  and liquid silicon.

For the previous calculation of the heat of the reaction  $\text{SiO}_{2(l)} \rightarrow \text{SiO}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$  it might appear preferable to use heat of reaction data based on this reaction directly. However, directly determined data such as those of Brewer and Mastick<sup>2</sup> and recalculated by Brewer and Edwards<sup>8, 19</sup> gives a greater uncertainty in the final heat of reaction. For example, these authors give  $\Delta H_0^{\circ} = 186,578 \pm 2,700$  calorie/mole for the reaction  $\text{SiO}_{2(\text{crist})} \rightarrow \text{SiO}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$ . As a check on the earlier calculations and in order to show that the Brewer Mastick work is more uncertain, it is possible to calculate  $\Delta H_T$  for the first reaction above using the direct data of Brewer and Mastick in the following manner:

$$\Delta H_T = \Delta H_0^{\circ} + (H_T - H_0)_{\text{SiO}_{(g)}} + \frac{1}{2}(H_T - H_0)_{\text{O}_{2(g)}} - (H_T - H_0)_{\text{SiO}_{2(l)}} \text{ referred to cristobalite at } 0^{\circ}\text{K} .$$



TABLE V

SUMMARY OF COMPONENT UNCERTAINTIES OF THE HEAT OF REACTION

All units are calorie/mole.

Uncertainties	<u>2,000 K</u>	<u>2,500 K</u>	<u>3,000 K</u>
$\Delta H_{\text{of}}^{\circ} \text{SiO}_{(\text{g})}$	$\pm 574 (2,000)**$	$\pm 574 (2,000)**$	$\pm 574 (2,000)**$
$\Delta H_{2000\text{f}} \text{SiO}_{2(\text{l})}$	$\pm 1,000$	$\pm 1,000$	$\pm 1,000$
$(H_{\text{T}} - H_{\text{b}}) \text{SiO}_{(\text{g})}$	$\pm 150$	$\pm 200$	$\pm 250$
$(H_{\text{T}} - H_{2000}) \text{SiO}_{2(\text{l})}$	0	$\pm 500$	$\pm 1,000$
$(H_{2000} - H_{\text{b}}) \text{Si}_{(\text{l})}$	$\pm 460$	$\pm 460$	$\pm 460$
$\frac{1}{2}(H_{\text{T}} - H_{\text{b}}) \text{O}_{2(\text{g})}$	$\pm 80$	$\pm 100$	$\pm 125$
	<hr/>	<hr/>	<hr/>
	$\pm 2,264(3,690)**$	$\pm 2,834(4,260)**$	$\pm 3,409(4,835)**$

\*Combined uncertainty of last two terms of equation used.

\*\*Coughlin's estimate of uncertainty in  $\Delta H_{\text{f}}(\text{SiO})$ , shown in parenthesis, is greater than that of Brewer and Edwards.

Values of  $(H_T - H_0)_{\text{SiO}_2(g)}$  and  $(H_T - H_0)_{\text{O}_2(g)}$  have already been obtained and listed in Table III. The heat content of liquid  $\text{SiO}_2$  relative to cristobalite at  $0^\circ \text{K}$ , can be obtained from the relation

$$(H_T - H_0)_{\text{SiO}_2(l)} = (H_T - H_{2000})_{\text{SiO}_2(l)} + \Delta H_{\text{fusion of cristobalite}} + (H_{2000} - H_{298})_{\text{crist.}} + (H_{298} - H_0)_{\text{crist.}}$$

which can be evaluated as follows:

$$(H_T - H_{2000})_{\text{SiO}_2(l)} = 21,660 \pm 1,000 \text{ calorie/mole (from Table I.)}$$

$$\Delta H_{\text{fusion}} = 2,500 \pm 500 \text{ calorie/mole (see earlier discussion)}$$

$$(H_{2000} - H_{298})_{\text{crist.}} = 28,120 \pm 600 \text{ calorie/mole (K. K. Kelley}^{13})$$

$$(H_{298} - H_0)_{\text{crist.}} = 1,667 \pm 50 \text{ calorie/mole (Edwards}^{19})$$

$$(H_T - H_0)_{\text{SiO}_2(l)} \text{ referred to cristobalite at } 0^\circ \text{K} = 53,947 \pm 2,150 \text{ calorie/mole}$$

Substituting the latter into the expression for  $\Delta H_T$ , we find that  $\Delta H_{3000} = 170,621 \pm 5,225$ .

This value of the heat of reaction agrees well with our previous value of  $\Delta H_{3000} = 171,513 \pm 3,400$  calorie/mole. However, the earlier data of Table IV have a smaller uncertainty and are used for subsequent calculations.

#### 4. Total Heat of Decomposition

The total heat, which can be absorbed by fused silica when it decomposes at  $3,000^\circ \text{K}$  by the reaction  $\text{SiO}_2(l) \rightarrow \text{SiO}(g) + \frac{1}{2}\text{O}_2(g)$ , is now computed as follows:

$$(H_{2000} - H_{298})_{\text{SiO}_2(\text{glass})} = 29,010 \text{ calorie/mole (Kelley}^{13})$$

$$(H_{3000} - H_{2000})\text{SiO}_2(\text{liq or glass}) = 21,660 \text{ calorie/mole (Table I)}$$

$$\Delta H_{3000} \text{ for } \text{SiO}_2 \rightarrow \text{SiO}_{(g)} + \frac{1}{2}\text{O}_2 = 171,513 \text{ calorie/mole (Table IV)}$$

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$$\begin{array}{l} \text{Total heat of decomposing } \text{SiO}_{2(\text{glass})} \\ \text{at } 3,000^\circ \text{ K starting from } \\ 298^\circ \text{ K.} \end{array} = 222,183 \text{ calorie/mole}$$

$$\begin{array}{l} \text{The equivalent value in other} \\ \text{units at } 4,940^\circ \text{ F starting from} \\ 77^\circ \text{ F is} \end{array} = 6,650 \text{ Btu/lb}$$

## B. ENTROPY CHANGE

Stull and Sinke<sup>25</sup> give the absolute entropy of  $\text{O}_{2(g)}$ . In Table II are given the entropy data for  $\text{SiO}_{(g)}$ . Kelley<sup>9</sup> gives the entropy of  $\text{SiO}_{2(\text{glass})}$  at  $298^\circ \text{ K}$  as  $S_{298} = 11.2 \pm 0.4 \text{ eu}$ . For higher temperatures Kelley<sup>13</sup> gives  $S_{2000} - S_{298} = 29.87 \text{ eu}$ . Thus  $S_{2000}^\circ = 41.07 \text{ eu}$ . In order to obtain entropy data for  $\text{SiO}_{2(l)}$  above  $2,000^\circ \text{ K}$ , we have had to use our estimated heat capacity data ( $C_p = 21.66 \text{ calorie/mole degree}$ ). The results of these calculations are shown in Table VI.

## C. FREE ENERGY CHANGE

Having obtained the heat of reaction and the entropy change in the previous sections, it is now possible to calculate the free energy change from the relation

$$\Delta F = \Delta H - T \Delta S.$$

The results of this calculation are shown in Table VII.

For  $\Delta H$ , the uncertainties represent maximum estimates. In estimating the uncertainties in  $\Delta F$  from the data in Table IV, the uncertainties of  $\Delta H$  and  $T \Delta S$  do not add algebraically. Actually, those uncertainties cancel in part by the use of consistent heat capacity data as discussed in the following paragraphs so that the value given at  $3,000^\circ \text{ K}$  is probably good to about  $\pm 4,000 \text{ calories/mole}$ , depending again on the uncertainty of the heat of formation of  $\text{SiO}_{(g)}$ .

TABLE VIENTROPY CHANGE FOR THE REACTION  $\text{SiO}_{2(l)} \rightarrow \text{SiO}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$ Temperature in Degrees Kelvin

		<u>2,000° K</u>	<u>2,500° K</u>	<u>3,000° K</u>	<u>Ref.</u>
$\frac{1}{2}\text{SO}_{2(g)}$	(e. u.)	32.11 ± .02	33.13 ± .02	33.99 ± .03	2
$S_{\text{SiO}_{(g)}}$	(e. u.)	66.04 ± 0.1	68.04 ± .1	69.67 ± .1	Table II
$S_{\text{SiO}_{2(l)}}$	(e. u.)	41.07 ± 0.6	46.13 ± 0.8	50.03 ± 1.0	1.9 at 2,000° K calculated using $C_p = 21.66$ calorie/mole · K for $T >$ 2,000° K
$\Delta S_T$	(e. u.)	57.08 ± 0.7	55.04 ± 0.9	53.63 ± 1.1	
$T\Delta S$	calorie/mole	114,160 ± 1,400	137,600 ± 2,250	160,890 ± 3,300	

TABLE VIIFREE ENERGY CHANGE FOR THE REACTION  $\text{SiO}_{2(l)} \rightarrow \text{SiO}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$ 

		<u>2,000° K</u>	<u>2,500° K</u>	<u>3,000° K</u>
$\Delta H$	(calorie/mole)	179,065 ± 3,700	174,926 ± 4,300	171,513 ± 4,800
$-T\Delta S$	(calorie/mole)	-114,160 ± 1,400	-137,600 ± 2,250	-160,890 ± 3,300
$\Delta F$	(calorie/mole)	64,905 ± 3,000	37,326 ± 3,500	10,623 ± 4,000

The variation of the above free energy data with temperature can be represented with sufficient accuracy by a straight line such as

$$\Delta F_T = 173,000 - 54.2 T \text{ (calorie/mole)}$$

which is valid for the temperature range of 2,000° K to 3,000° K and accurate to  $\pm 4,000$  calorie/mole at 3,000° K. The values from this equation fit the calculated points of Table VII sufficiently well that it can be used for the sake of simplicity in our applications. This linear equation can also be used to extrapolate slightly beyond the temperature range of the data. (2,000 - 3,000° K)

In assessing the accuracy of the free energy expression which we have obtained, we may take as a second trial a heat capacity for liquid  $\text{SiO}_2^{(1)}$  of 20.66 calorie/mole  $\cdot$  K instead of the 21.66 calorie/mole  $\cdot$  K as in our earlier calculations. With such a value of heat capacity, the heat of formation of  $\text{SiO}_2^{(1)}$  at 3,000° K would be  $\Delta H_{3000}^\circ = -211,467$  (instead of -210,467) calorie/mole. In Table IV use of this value of  $\Delta H_{3000}^\circ, \text{SiO}_2^{(1)}$  will raise the heat of the reaction to  $\Delta H \left[ \text{SiO}_2^{(1)} \rightarrow \text{SiO}_{(g)} + \frac{1}{2} \text{O}_{2(g)} \right] = 172,513$  calorie/mole (instead of 171,513). Next, from Table VI it can be seen that the entropy of  $\text{SiO}_2^{(1)}$  would be lowered by the use of the smaller  $C_p$  value by an amount equal to  $\Delta S_{\text{SiO}_2^{(1)}} = 0.41$  e. u. This would make  $\Delta S_{\text{SiO}_2, 3,000^\circ \text{K}} = 49.62$  e. u. (instead of 50.03 e. u.). Consequently, the  $\Delta S$  of reaction at 3,000° K would be increased to 54.04 e. u. (instead of 53.63 e. u.), and  $(T\Delta S)_{3000^\circ \text{K}} = 162,120$  calorie (instead of 160,890 calorie). The corresponding free energy value is  $\Delta F_{3,000^\circ \text{K}} = 10,393$  calorie/mole instead of the 10,623 calorie/mole obtained with  $C_p = 21.66$  calorie/mole  $\cdot$  K or a decrease below the previous value of 230 calorie/mole. The lower  $C_p$  value for  $\text{SiO}_2$  indicates a slightly increased vapor pressure.

It is seen from the above discussion that the free energy does not change too rapidly with changes in the value of the heat capacity of liquid silica although its components, the heat of reaction, and the entropy do. This can be shown by the following more general treatment.

To estimate the accuracy of our free energy functions, we need to reconsider in detail how they were calculated. The discussion is based on the fundamental definition,

$$\Delta F = \Delta H - T\Delta S \quad . \quad (6)$$

In considering the reaction



we have noted that at 2,000° K the free energy change is accurate to about  $\pm 3,000$  calories/mole. This is the uncertainty estimated from Coughlin's table. Of this uncertainty about 2,000 calorie/mole is associated with contributions from the formation of  $\text{SiO}(g)$  and 1,000 calorie/mole is associated with the formation of liquid  $\text{SiO}_2$ . To make a rough estimate of the errors to be expected at higher temperatures, we can modify the fundamental equation to obtain

$$\Delta F = \Delta H_{2000} + \int_{2000}^T \Delta C_p dT - T \left( \Delta S_{2000} + \int_{2000}^T \frac{\Delta C_p}{T} dT \right)$$

$$= \Delta H_{2000} - 2000 \cdot \Delta S_{2000} - (T-2000) \Delta S_{2000}$$

$$+ \int_{2000}^T \Delta C_p dT - T \int_{2000}^T \frac{\Delta C_p}{T} dT$$

If we now designate the first two terms of this last equation as  $\Delta F_{2000}$  and replace our variable of integration  $T$  by  $r$ , the dummy variable (to avoid confusion with the  $T$  used as the limit of our integration) we obtain

$$\Delta F = \Delta F_{2000} - (T-2000) \Delta S_{2000} + \int_{2000}^T \Delta C_p dr - T \int_{2000}^T \frac{\Delta C_p}{r} dr$$

$$= \Delta F_{2000} - (T - 2000) \Delta S_{2000} + T \int_{2000}^T \left( \frac{\Delta C_p}{T} - \frac{\Delta C_p}{r} \right) dr .$$

The uncertainty in  $\Delta F_{2,000}$  is  $\pm 3,000$  calorie/mole according to our earlier estimate. Since the value of  $\Delta S_{2,000} = 57.08 \pm 0.7$  e.u., the uncertainty in the second term at  $3,000^\circ \text{K}$  is  $\pm 700$  calorie/mole. The last integral would also contribute to the overall uncertainty if  $\Delta C_p$  for the reaction were in error. For the present case, we may get a rough order of magnitude of this uncertainty if we note that

$C_p$  for  $\frac{1}{2} \text{O}_2 \cong 4.5$  calorie/mole degree,  $C_{p\text{SiO}} = 9.0$  calorie/mole degree, and  $C_{p\text{SiO}_2} = 21.66$  calorie/mole degree. Hence,  $\Delta C_p \cong -8.0$  calorie/mole degree. The most likely source of error in  $\Delta C_p$  is  $C_{p\text{SiO}_2}$ . If this error were 1 calorie/mole degree so that actually  $C_{p\text{SiO}_2} = 20.66$  and  $\Delta C_p = -7.0$ , then the total error would amount to an additional 220 calorie/mole. Thus at  $3,000^\circ \text{K}$  the uncertainties in  $\Delta F$  add up to 3,920 or 4,000 calorie/mole.

As a further check on the free energy equation which we have obtained, we can compare values of the free energy at  $2,000^\circ \text{K}$  with those tabulated by Coughlin.<sup>3</sup> He gives  $\Delta F_{2,000}^{\text{SiO(g)}} = -59,200$  calorie/mole and  $\Delta F_{2,000}^{\text{SiO}_2(1)} = -123,900$  calorie/mole from which we get for the reaction  $\text{SiO}_{2(1)} \rightarrow \text{SiO(g)} + \frac{1}{2} \text{O}_{2(g)}$  the free energy change

$$\Delta F_{2,000} = 64,700 \pm 3,000 \text{ calorie/mole}$$

This compares favorably with our value of 64,600 calorie/mole based on the empirical formula.

In figure 1 are plotted the free energy data obtained by the present calculations. The empirical equation has been extrapolated above  $3,000^\circ \text{K}$ . This can be safely done over a narrow temperature range and will be a fair approximation at higher temperatures. From the expression

$$\Delta F = \Delta H - T\Delta S ,$$

with a reference temperature of 3,000° K, we find

$$\Delta F_T = \Delta H_{3,000} + \int_{3,000}^T \Delta C_p dT - T\Delta S_{3,000} - T \int_{3,000}^T \frac{\Delta C_p dT}{T}$$

where  $\Delta C_p$  is equal to the change in heat capacity of the reaction considered, i. e.,

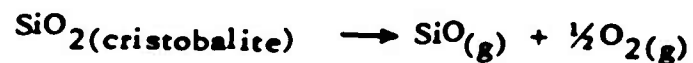
$$\Delta C_p = \frac{1}{2}C_{pO_2} + C_{pSiO} - C_{pSiO_2(1)}$$

For small temperature intervals, the second and fourth terms in the free energy equation will cancel, thus justifying the extrapolation,

$$\Delta F_T = \Delta H_{3,000} - T\Delta S_{3,000} .$$

For temperatures below 2,000° K, where solid  $SiO_2$  is the stable phase, the data of Coughlin<sup>9</sup> for cristobalite have also been plotted in figure 1. In this case his tabulated free energies of formation for  $SiO_2$  and  $SiO(g)$  can be subtracted and used directly.

It is also possible to develop an empirical free energy equation for the immediate range below 2,000° K, by the use of entropy data. For example, for the reaction



we get

$$S_{\text{cristobalite}; 2,000^\circ K} = S_{298^\circ K} + (S_{2,000^\circ K} - S_{298^\circ K}) = 40.04 \text{ e.u. } 13,14 .$$

$$\frac{1}{2}S_{O_2; 2,000^\circ K} = 32.11 \text{ e.u.}$$

$$S_{SiO 2,000^\circ K} = 66.04 \text{ e.u.}$$



and

$$\Delta S_{2,000^\circ K} = S_{SiO} + \frac{1}{2} S_{O_2} - S_{SiO_2} = 58.11 \text{ e.u.}$$

Using this value of the entropy change at  $2,000^\circ K$ , we can now fit a curve through the  $2,000^\circ K$  point, since  $\Delta F_{2,000} = 64,600$  calorie/mole from our previous formula. Hence,

$$\Delta F^\circ = 180,800 - 58.11 T \text{ (calorie/mole for } 1,800 < T < 2,000^\circ K)$$

The above relation gives  $\Delta F_{1,800}^\circ = 76,200$  calorie/mole and  $\Delta F_{1,900}^\circ = 70,390$  calorie/mole. These values can be compared with values calculated from Coughlin's data

$$\Delta F_{1,800}^\circ = 76,450 \text{ calorie/mole}$$

$$\Delta F_{1,900}^\circ = 70,650 \text{ calorie/mole.}$$

This good agreement increases our confidence in the data and calculations.

#### D. EQUILIBRIUM CONSTANT

For the evaluation of the equilibrium constant corresponding to the reaction that is the subject of Section II, the usual relation  $\Delta F^\circ = -RT \ln K$  can be modified to give

$$\log_{10} K = \frac{-\Delta F}{2.303RT} = \frac{\Delta H}{4.57T} + \frac{\Delta S}{4.57}$$

For the present case, this becomes

$$\log_{10} K = \frac{-37,900}{T} + 11.85$$

This equilibrium constant has been plotted in figure 2 as a function of  $1/T$ . It can be seen that at higher temperatures, the equilibrium constant becomes larger.

## E. EQUILIBRIUM VAPOR PRESSURE

In the range 2,000 - 3,000° K we have shown that the standard free energy of the reaction  $\text{SiO}_{2(l)} \rightleftharpoons \text{SiO}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$  can be represented as a function of temperature by

$$\Delta F_T^\circ = 173,000 - 54.2T.$$

This is related to the equilibrium constant, K by the conventional definition

$$\Delta F_T^\circ = -RT \ln K = -RT \ln \frac{a_{\text{SiO}_{(g)}} a_{\text{O}_{2(g)}}^{\frac{1}{2}}}{a_{\text{SiO}_{2(l)}}}$$

where  $a_i$  = activity of component (or the fugacity in case of gaseous components). For liquid  $\text{SiO}_{2(l)}$ , the usual assumption is made that the activity is unity, i.e., any solution effects of  $\text{SiO}_{(g)}$ ,  $\text{O}_{2(g)}$  or other equilibrium species in  $\text{SiO}_2$  are considered negligible.

For the gaseous components, it is reasonable to replace the activities by partial pressures of the species being considered as long as the gases do not deviate markedly from the perfect gas laws. This assumption is valid at low-pressures and high-temperatures. For oxygen (fugacity = 48 atm at pressure of 50 atm and 0°C, <sup>61</sup> critical temperature,  $T_c = 154.3^\circ\text{K}$ , critical pressure,  $P_c = 49.7\text{ atm}$ ) at

50 atm and 2,000° K the reduced temperature is  $T_R = \frac{T}{T_c} = 12.95$ , and the reduced pressure  $P_r = P/P_c = 0.995$ . For this case <sup>34</sup>  $f/P = 1.0 +$  and the fugacity is essentially equal to the pressure.

For  $\text{SiO}_{(g)}$ , whose condensed properties are practically unknown, we must use some very rough approximations to estimate  $P_c$  and  $T_c$ . Hirschfelder *et al* <sup>62</sup> list some rough empirical rules which can be used in this case. Using the condition that the melting temperature is  $2/5$ , and the fact that Edwards <sup>19</sup> states that the melting point of  $\text{SiO}$  must be greater than 1,975° K, we calculate  $T_c \approx 5,000^\circ\text{K}$ . To estimate the molar volume at the critical point, we note that  $\tilde{V}^{\text{sol}} = 0.321 \tilde{V}_c$ . According to Edwards <sup>19</sup> the density of solid  $\text{SiO}$  is about 2.15 gm/cm<sup>3</sup> (20.5 cm<sup>3</sup>/mole). Making the assumption that the molar volume of  $\text{SiO}$  at its

melting point is equal to the molar volume ( $20.5 \text{ cm}^3/\text{mole}$ ) given by Edwards, we find a molar volume at the critical point of  $\tilde{v}_c = 64.0 \text{ cm}^3/\text{mole}$ . Finally, from the fact that many molecules have a compressibility factor of 0.292 (Hirschfelder et al)<sup>62</sup>, we find that  $p_c = 1,870 \text{ atm}$ . At 50 atm. and  $2,000^\circ \text{ K}$ ,  $p_r = 0.0267$ , and  $T_R = 0.4$ . Again, estimating from the Hougen and Watson chart, it is found that  $f/p \cong 0.95$ . In view of the uncertainties involved in the above calculations, the results must be considered very approximate. However, they do indicate that in the pressure range of interest (1-50 atm) and from  $2,000 - 3,000^\circ \text{ K}$ , the gas will behave ideally. For further considerations, pressures will be used instead of fugacities.

Using the simplifying assumptions discussed above, we get for the final formulas

$$\Delta F_T^0 = -RT \ln P_{\text{SiO}} P_{\text{O}_2}^{1/2} = -RT \ln K_{\text{eq}} ,$$

or

$$P_{\text{SiO}} P_{\text{O}_2}^{1/2} = e^{-\frac{\Delta F^0}{RT}} = e^{-\frac{173,000}{RT}} e^{\frac{54.2}{R}} .$$

Under neutral conditions,  $P_{\text{SiO}} = 2P_{\text{O}_2}$

and

$$P_{\text{SiO}} = e^{18.41 \left(1 - \frac{3160}{T}\right)} .$$

The vapor pressure data for this equation are presented as the upper curve in figure 3. It gives a partial pressure of 0.667 atm for  $\text{SiO}_{(g)}$  at  $3,085^\circ \text{ K}$  (Boiling point under neutral conditions, neglecting other reactions). It should also be noted that

$$P_{\text{total}} = 1.5 P_{\text{SiO}} = 1.5 e^{18.41 \left(1 - \frac{3160}{T}\right)} .$$

The vapor pressure of  $\text{SiO}_{(g)}$  in equilibrium with condensed  $\text{SiO}_2$  is plotted for a large temperature range in figure 4. The principal curve in this figure is based on the single reaction given and neglects all other equilibria.

For the case of  $\text{SiO}_2$  decomposing in the presence of air,

$$P_{\text{N}_2} = 4(P_{\text{O}_2} - P_{\text{SiO}})$$

and

$$P_{\text{total}} = P_{\text{N}_2} + P_{\text{SiO}} = \text{constant} = 5P_{\text{O}_2} - P_{\text{SiO}}$$

From the above relation for  $P_{\text{SiO}} P_{\text{O}_2}^{1/2}$

we now find

$$P_{\text{SiO}} (P_{\text{total}} + P_{\text{SiO}})^{1/2} = e^{28.0 (1 - \frac{3110}{T})}$$

These data have been plotted in figures 3 and 4 for the two cases,  $p = 1 \text{ atm}$ , and  $p = 10 \text{ atm}$ .

It can be seen from the above equations that the presence of the oxygen suppresses the  $\text{SiO}$  gas formation. It should also be emphasized that the data here presented assumes only the reaction  $\text{SiO}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$  to be important.

Dissociation of oxygen has been neglected here but is included in later discussions. Nitrogen is considered to be an inert gas.

For temperatures below  $2,000^\circ \text{K}$  the relation for the vapor pressure  $P_{\text{SiO}}$  must be modified. Using the relation  $\Delta F^\circ = 180,800 - 58.11 T$  for  $(1,800^\circ \text{K} < T < 2,000^\circ \text{K})$

we get

$$P_{\text{SiO}} = e^{\frac{19.72 (1 - \frac{3975}{T})}{T}}$$

A curve for this function has been plotted in figure 5 over the temperature range (1,800 - 2,000° K). For comparison purposes the available experimental data have also been plotted. The effusion cell measurements of Brewer and Mastick are seen to agree well with the calculated data. The mass spectrometric measurements of Porter *et al*<sup>3</sup> are high by a factor of about 6. Porter *et al*<sup>3</sup> indicated in their paper and in private communications that their absolute values of pressures could be in error by a factor of 2 or 3. A point of possible uncertainty in the work of Porter *et al* is the fact that they used some older vapor pressure data from Brewer.<sup>36</sup> They had calibrated their equipment by assuming that  $p_{Ag}^{107} = 1 \times 10^{-6}$  atm at 1,245° K, and that  $p_{Au} = 2 \times 10^{-5}$  atm at 1,750° K. However, more recent work by Honig<sup>37</sup> gives values of  $1.85 \times 10^{-6}$  atm for  $Ag^{107}$ , and  $7.9 \times 10^{-5}$  atm for Au. All observed pressures of the various species are then increased for the appropriate temperature range by the ratios 1.85/1 and 7.9/2.0. It is not completely clear that the pressures should be increased by this much since Porter *et al*<sup>3</sup> state that they checked their calibration by the vaporization of a weighed amount of Ag or Au.

To compare their data further with the present results, we have shown in Table VII-A free energy data calculated from their observed vapor pressures. It is seen that the results based on their tabulated pressures are in good agreement with our free energy data. It should also be noted that their reaction does not correspond to stoichiometric conditions. They apparently did not have neutral conditions. The free energy data, based on recalculated vapor pressures, are in poorer agreement with our calculated free energy curve given in figure 1. Further evidence that Porter's tabulated data are probably preferable will be produced when the dissociation of oxygen is considered in a following section.

In the literature given by Inuzuka and Ageha<sup>38</sup> are some additional vapor pressure data for  $SiO_2$ . They report a vapor pressure of  $1.1 \times 10^{-7}$  atm for  $SiO_2$  at 1,200° C (1,473° K). They used a "Mo and W wire" to heat a fused  $SiO_2$  tube and measured the vapor pressure by a Langmuir method. At this temperature our thermochemical calculations give a total vapor pressure of  $6 \times 10^{-10}$  atm (See fig. 4), a discrepancy by a factor of 180. However, it is shown in the following arguments that they were actually studying some other reaction, possibly the following:

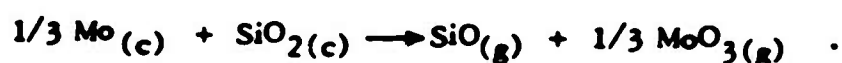


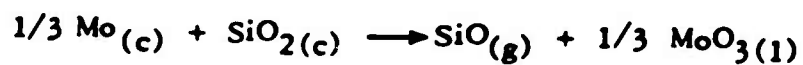
TABLE VII-A

· COMPARISON OF FREE ENERGIES BASED ON DATA OF PORTER et al <sup>3</sup>

<u>1,800° K</u>	<u>P<sub>SiO</sub>(atm)</u>	<u>P<sub>O<sub>2</sub></sub>(atm)</u>	<u>ΔF<sub>(calcd)</sub></u> <u>(calorie/mole)</u>	<u>ΔF<sub>(our curve)</sub></u> <u>(calorie/mole)</u>
Porter data, as is	6.8 x 10 <sup>-6</sup>	5.2 x 10 <sup>-8</sup>	72,400	76,000
Porter data, corrected	2.68 x 10 <sup>-5</sup>	2.05 x 10 <sup>-7</sup>	65,100	
<u>1,900° K</u>				
Porter data, as is,	3.4 x 10 <sup>-5</sup>	8.2 x 10 <sup>-8</sup>	69,595	71,000
Porter data, corrected	1.34 x 10 <sup>-4</sup>	32.4 x 10 <sup>-8</sup>	61,800	

This reaction would tend to give a higher vapor pressure of SiO<sub>(g)</sub> than expected under neutral conditions. The presence of W might also reduce SiO<sub>2</sub>, but it would not be expected to change the calculated pressure due to Mo by <sup>2</sup> more than a small factor.

To obtain thermochemical data for the suspected reaction with Mo, we can first use the free energy data of Coughlin for the reaction to give liquid MoO<sub>3</sub>, instead of the gaseous product



The free energy of this reaction is then

$$\begin{aligned} \Delta F_{1473} &= \Delta F_{\text{SiO}} + 1/3 \Delta F_{\text{MoO}_3} - \Delta F_{\text{SiO}_2} \\ &= 63,000 \text{ cal/mole} \end{aligned}$$

<sup>3</sup>Coughlin gives 1068°K as the melting point of MoO<sub>3</sub>.

Now it is necessary to estimate the free energy of vaporizing liquid  $\text{MoO}_3$ .



We can estimate that  $\Delta F_{1,530}^\circ = 0$  for the above vaporization process from the fact that the normal boiling point of  $\text{MoO}_3$  is  $1,530^\circ \text{K}$  according to Brewer<sup>39</sup>. This assumption is probably a conservative one because Berkowitz, Inghram, and Chupka<sup>7</sup> have shown that, at the boiling point, the species  $(\text{MoO}_3)_3$ ,  $(\text{MoO}_3)_4$ , and  $(\text{MoO}_3)_5$ , are probably most important. They indicate that the monomer is present in an amount less than a few percent at the temperature of their measurements (near  $900^\circ \text{K}$ ). On the other hand, Brewer and Elliott<sup>39, 40</sup> indicate that the monomer is probably the most important specie. For the present calculation we make the simplifying assumption that only the monomer is important. We therefore assume that  $\Delta F_{1,530}^\circ = 0$ . Actually, if polymers of  $\text{MoO}_3$  do exist at the normal boiling point, then  $\Delta F_{1,530}^\circ > 0$  for the above reaction.

We can now estimate the free energy change for vaporization by assuming Trouton's constant to be 21. Therefore  $\Delta F_{1473} = 400$  calorie/mole.

Now combining the last two reactions (liquid  $\text{MoO}_3$  formation and vaporization) we find for the overall, desired reaction:

$$\Delta F_{1,473^\circ \text{K}} = + 63,000 + 400 = 63,400 \text{ calorie/mole}$$

$$\text{Since } P_{\text{SiO}} \cdot P_{\text{MoO}_3}^{1/3} = e^{-\Delta F/RT}$$

we find

$$P_{\text{SiO}} = 1.24 \times 10^{-7} \text{ atm.}$$

$$P_{\text{MoO}_3} = .4 \times 10^{-7} \text{ atm.}$$

and

$$P_{\text{total}} = 1.65 \times 10^{-7} \text{ atm.}$$

This last value of that pressure is in good agreement with the value of  $1.1 \times 10^{-7}$  atm reported by Inuzuka<sup>38</sup>. The above discussion shows that he was not studying the vaporization of pure  $\text{SiO}_2$  in a neutral atmosphere and gives additional strength to the data used in the present report. Since Coughlin uses essentially the same heat of formation data for  $\text{SiO}_{(g)}$  as we used earlier, our recalculation of Inuzuka's results further substantiate that choice.

So far we have only considered one reaction in  $\text{SiO}_2$  decomposition as indicated in the title of this section of the report. Because fairly good agreement is obtained with experimental data in this manner, it appears probable that this reaction is the most important one. However, other additional competing or simultaneous reactions may also be important. These will now be considered in the following sections.



### III. THERMOCHEMISTRY OF THE REACTION $\text{SiO}_{(s)} \rightleftharpoons \text{SiO}_{(g)}$

The equilibrium between solid and gaseous SiO is of interest because of the possibility that  $\text{SiO}_{(s)}$  formation may limit the vapor pressure of  $\text{SiO}_{(g)}$  to be expected from the reactions discussed in the previous sections. Data concerning properties of solid SiO are very limited. According to Brewer and Edwards<sup>8,19</sup> and Hoch and Johnson,<sup>35</sup>  $\text{SiO}_{(s)}$  is unstable relative to  $\text{Si}_{(s)}$  and  $\text{SiO}_{2(s)}$  below 1,450° K and 1,573° K, respectively. However, above these temperatures the solid phase  $\text{SiO}_{(s)}$  does exist as shown by X-ray diffraction results.

The limited amount of thermodynamic data that are available for  $\text{SiO}_{(s)}$  are also very uncertain. Brewer and Edwards<sup>8</sup> have interpreted the results of Tombs and Welch<sup>23</sup> obtained over a mixture of Si and  $\text{SiO}_2$  as referring to the reaction  $\text{SiO}_{(s)} \rightleftharpoons \text{SiO}_{(g)}$  in the temperature range of (1,573° - 1,920° K). They state that for this temperature range  $\Delta H = 58,550$  calorie/mole and  $\Delta S = 25.45$  e. u., although they point out that the entropy data may be incorrect. If these data are used as stated, for free energy of reaction versus temperature, the approximate relation  $\Delta F = 58,550 - T \times 25.45$  is obtained. From this, one obtains  $p = 1$  atm ( $\Delta F = 0$ ) at  $T = 2,300^\circ \text{K}$ .

Additional vapor pressure data calculated from this relation are plotted in figure 6 by extrapolating to temperatures above 2,000° K. This extrapolation is not considered too good in view of the entropy uncertainty.

One can also utilize the above data in another, more correct extrapolation above 2,000° K. For this, the following data were taken from Brewer and Edwards:<sup>8,19</sup>

$$C_p(\text{crystalline SiO}) = 10.57 + 2.98 \times 10^{-3}T - 2.72 \times 10^5 T^{-2} ;$$

$$S_{298}^\circ(\text{SiO crystalline}) = 6.4 \text{ e.u.} ;$$

and  $S_{298}^\circ(\text{SiO amorphous}) = 7.3 \text{ e.u.}$

With these data we find that  $S_{2,000}^{\circ}(\text{SiO}_{\text{amorphous}}) = 31.1 \pm 3.0 \text{ e.u.}$

Using our earlier result that  $S_{2,000}^{\circ}(\text{SiO}_{(g)}) = 66.04 \text{ e.u.}$ , we find that for the present reaction  $\Delta S = 34.94 \text{ e.u.}$

If we now assume that the earlier relation  $\Delta F = 58,550 - 25.45 T$  is valid at  $T = 2,000^{\circ} \text{ K}$ , we can fit the equation at  $2,000^{\circ} \text{ K}$  with better entropy values to extrapolate to higher temperatures.

By using more realistic entropy values, we obtain

$$\Delta F = 77,530 - 34.94 T.$$

The above relation corresponds to a heat of reaction of  $\Delta H = 77,530$  calorie/mole in the temperature range near  $2,000^{\circ} \text{ K}$ . These data are plotted in figure 1. The line is dashed above  $2,000^{\circ} \text{ K}$ , because of the uncertainty in the data.

Using the data of Brewer<sup>39</sup> on the heat of formation of  $\text{SiO}_{(s)}$  ( $-104,600$  calorie/mole), we can estimate the heat of the reaction,  $\text{SiO}_{(s)} \rightarrow \text{SiO}_{(g)}$  as follows:

$$\begin{aligned} \Delta H_{298} &= \Delta H_{f\text{SiO}_{(g)}} - \Delta H_{f\text{SiO}_{(s)}} = -21,800 - (-104,600) \text{ calorie/mole} \\ &= +82,800 \text{ calorie/mole} \end{aligned}$$

Also,

$$\Delta H_T = \Delta H_{298} + \int_{298}^T \Delta C_p dT$$

$$\Delta H_T = \Delta H_{298} + (H_T - H_{298})_{\text{SiO}_{(g)}} - (H_T - H_{298})_{\text{SiO}_{(s)}}$$

$$= \Delta H_{298} + (H_T - H_0)_{\text{SiO}_{(g)}} - (H_{298} - H_0)_{\text{SiO}_{(g)}} - (H_T - H_{298})_{\text{SiO}_{(s)}}$$

Therefore,

$$\begin{aligned} \Delta H_{2,000} &= 82,800 + 8.18 \times 2,000 - 6.955 \times 298 - \int_{298}^{2,000} [10.57 + 2.98 \times 10^{-3}T - 2.72 \times 10^{-5}T^2] dT \\ &= 82,800 + 16,360 - 2,070 - 23,090 \end{aligned}$$

$$\Delta H_{2,000} = 74,000 \text{ calorie/mole.}$$

This value agrees well with the value of 77,530 calorie/mole given above, and thus makes the relation seem more reliable. Accordingly, the data for the relation  $\Delta F = 77,530 - 34.94 T$  have been taken as the best and have been plotted in figure 6.

These data lead to a larger vapor pressure of  $\text{SiO}_{(g)}$  in equilibrium with  $\text{SiO}_{(s)}$  than predicted by the first expression  $\Delta F = 58,500 - 25.45 T$ . However, the data show that the vapor pressure of  $\text{SiO}_{(s)}$ , based on either expression, is much greater than the vapor pressure of  $\text{SiO}_{(g)}$  in equilibrium with  $\text{SiO}_{2(s)}$  under neutral conditions. It would, therefore, not be expected that  $\text{SiO}_{(s)}$  could be formed from  $\text{SiO}_{2(s)}$  under neutral conditions.

#### IV. ASSOCIATION REACTIONS

Very little information is available regarding the formation of dimers and trimers of  $\text{SiO}_{(g)}$ . The paper of Porter, Chupka, and Inghram<sup>3</sup> gives one measurement of the  $\text{Si}_2\text{O}_2$  pressure in equilibrium with  $\text{SiO}_{(g)}$ . These pressures are  $4.5 \times 10^{-8}$  atm. and  $1.1 \times 10^{-4}$  atm., respectively, at  $1,463^\circ \text{K}$ .

From this it follows that  $K_{eq} = \frac{P_{\text{Si}_2\text{O}_2}}{P_{\text{SiO}}^2} = 3.72$  at  $1,463^\circ \text{K}$ .

From the above equilibrium constant, we can calculate that the free energy change for dimerization is  $\Delta F_{1,463} = -3,820$  calorie/mole of  $\text{Si}_2\text{O}_2(g)$ . To get a very rough estimate of the degree of dimerization at higher temperatures, it is necessary to estimate the entropy change for the above reaction. Data are already available for the entropy of the monomer,  $\text{SiO}_{(g)}$ . For the dimer, however, no molecular data are available, and its entropy must be estimated by approximation methods.

The empirical equation of Kubaschewski and Evans<sup>15</sup> can be used to estimate  $S_{298} = 64.1$  e.u. for  $\text{Si}_2\text{O}_2(g)$ . Assuming that the  $\text{Si}_2\text{O}_2(g)$  has about the same entropy increment as another four-atom molecule,  $\text{ClF}_3$ , whose entropy increment is  $S_{1,500} - S_{298} = 29.5$  e.u. (according to the NBS Series III<sup>41</sup> tabulation), we get  $S_{1,500} = 93.6 \pm 3.0$  e.u. for  $\text{Si}_2\text{O}_2(g)$ , where the uncertainty is only estimated. From the tables of Edwards<sup>19</sup> we find that  $S_{1,500}^{\text{SiO}(g)} = 63.5$  e.u.; and hence for the reaction as given

$$\Delta S = 93.6 - 2(63.5) = -33.4 \text{ e.u.}$$

Assuming that  $\Delta S_{1,500} = \Delta S_{1,463}$ , and using the relation  $\Delta F_T = \Delta H_{1,463} - T \Delta S_{1,463}$ , we find that  $\Delta H_{1,463} = -52,500$  calorie/mole  $\text{Si}_2\text{O}_2(g)$ . From this we find that  $\Delta F_T = -52,500 + 33.4 T$ . This relation is, of course, very rough and at an extrapolated temperature of  $3,000^\circ \text{K}$  the uncertainty may be  $\pm 5,000$  calorie/mole or more. The free energy change for the reverse reaction is shown in figure 1.

At  $3,000^\circ \text{K}$ , a free energy change of  $+47,700$  calories/mole is obtained from the above equation, corresponding to an equilibrium constant of  $3.46 \times 10^{-4}$ . The expected pressure of  $\text{Si}_2\text{O}_2$  as a function of  $\text{SiO}$  pressure is presented in Table VIII.

TABLE VIII

PRESSURES OF  $\text{Si}_2\text{O}_2(\text{g})$  IN EQUILIBRIUM WITH  $\text{SiO}(\text{g})$  AT 3,000 K

<u><math>P_{\text{SiO}} \text{ (atm)}</math></u>	<u><math>P_{\text{Si}_2\text{O}_2} \text{ (atm)}</math></u>
0.4	$5.55 \times 10^{-5}$
1	$3.46 \times 10^{-4}$
10	$3.46 \times 10^{-2}$
100	3.46 atm.

The data in Table VIII shows that the dimerization effect is probably not too important for the case where the boiling point is above 3,000° K and the ambient pressures are less than 50 atms. However, the dimerization phenomenon would be more important (for a given pressure of  $\text{SiO}$  ) at lower temperatures. Again, it should be emphasized that these data do not have high accuracy.

## V. OXYGEN DISSOCIATION

Because of the fact that dissociation of oxygen may lead to a higher effective pressure in an equilibrium mixture of  $\text{SiO}_2$ , which is decomposing to form  $\text{SiO}_{(g)}$  and  $\text{O}_{2(g)}$ , a brief review of the dissociation of  $\text{O}_2$  in the temperature range of  $2,900 - 3,100^\circ \text{K}$  has been made. The data of Stull and Sinke<sup>25</sup> have been used in the present case. It was necessary to extrapolate the free energy data from  $3,000^\circ \text{K}$  to  $3,100^\circ \text{K}$  to obtain an equilibrium constant at the higher temperature. (The extrapolated data agree with the earlier NBS Series III<sup>41</sup> data.) The values of the equilibrium constants obtained are shown in Table IX.

TABLE IX  
EQUILIBRIUM CONSTANTS FOR THE REACTION  $\frac{1}{2}\text{O}_{2(g)} \rightleftharpoons \text{O}_{(g)}$

Temperature (° K)	$K = \frac{P_{\text{O}}}{P_{\text{O}_2}^{1/2}}$
2,900	0.079
3,000	0.112
3,100	0.157

From the equilibrium constants shown in Table IX, values of the  $P_{\text{O}_2}/P_{\text{O}}$  ratio have been obtained for various selected oxygen pressures. The results of these calculations are plotted in figure 7 where it is seen that at an oxygen pressure of 0.01 atm at  $2,960^\circ \text{K}$  the pressure of oxygen atoms, in equilibrium, is also about 0.01 atm. For the case of 0.333 atm  $\text{O}_2$  at  $3,100^\circ \text{K}$ , there will be an atomic oxygen pressure of  $P_{\text{O}_{(g)}} = 0.09 \text{ atm}$ . The dissociation of  $\text{O}_{(g)}$  will contribute a significant (although smaller) amount to the total pressure in the case of decomposition of  $\text{SiO}_2$  to  $\text{SiO}$  and  $\text{O}_2$  near  $3,100^\circ \text{K}$ .

To cover an even wider temperature range, the data of Stull and Sinke below  $3,000^\circ \text{K}$  and of the NBS above  $3,000^\circ \text{K}$  have been used to obtain the free energy change and equilibrium constants for the dissociation reaction. To get an approximate linear relation for the free energy change of the reaction at  $3,000^\circ \text{K}$ , the data of Stull and Sinke<sup>25</sup> was used. From their heat of reaction and entropy data, the following relation is obtained:  $\Delta F = 61,348 - 16.11 T$ . This relation gives a free energy change of 29,129 calorie/mole at  $2,000^\circ \text{K}$ , whereas Stull and Sinke's<sup>25</sup> tabulation gives 29,091 calorie/mole. The above free energy relation and the corresponding equilibrium constants are plotted in figures 1 and 2.

The data on the dissociation of oxygen are well known and provide a test of the reliability of the  $\text{SiO}_2$  decomposition data reported by Porter et al, inasmuch as their mass spectrometric measurements included both  $\text{O}_2$  and  $\text{O}$ . At 1,900° K they give

$$P_{\text{O}} = 2.2 \times 10^{-7} \text{ atm. and } P_{\text{O}_2} = 8.2 \times 10^{-8} \text{ atm.}$$

for the reaction  $\frac{1}{2}\text{O}_2 \rightarrow \text{O}_{(\text{g})}$ . This corresponds to

$$K_{1,900} = 7.7 \times 10^{-4} = \frac{P_{\text{O}}}{P_{\text{O}_2}^{1/2}}$$

Hence  $\Delta F_{1,900} = 27,065$  calorie/mole  
Stull and Sinke<sup>25</sup> give

. For the same dissociation reaction,

<u>Temperature, ° K</u>	<u>Log<sub>10</sub>K</u>	<u><math>\Delta F^\circ</math>, calorie/mole</u>
1,900	-3.529	30,678
2,000	-3.178	29,091
2,100	-2.859	27,477

Thus, we see that Porter's free energy value of 27,065 calorie/mole, based on his reported pressure measurements, is low by 3,613 calorie/mole at 1,900° K.

If we had attempted to correct Porter's vapor pressures by using the more recent gold vapor pressure data, then the pressures would have been increased by a factor of 3.95. This would increase the equilibrium constant at 1,900° K to a value of  $\log_{10}K = -2.815$ , thus making the standard free energy change  $\Delta F_{1,900} = 24,400$  calorie/mole.

However, this value is in error by 6,300 calories at 1,900° K, whereas the actual value reported by Porter, et al, is in error by only 3,600 calories/mole. Therefore, it seems that there may have been either compensating errors in Porter's reported data, in their choice of cross sections, or the newer gold vapor pressure data may be in error. In any case, at this time it appears more logical to accept Porter's tabulated pressure data as being correct because it yields free energy values in better agreement with the known values on the  $\text{O}_2$  dissociation reaction.

## VI. THERMOCHEMISTRY OF THE REACTION $\text{SiO}_{(g)} \rightarrow \text{Si}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$

To estimate the importance of the  $\text{SiO}$  dissociation reaction to yield  $\text{Si}_{(g)}$  we can use the following free energy and entropy of formation data at  $3,000^\circ \text{K}$ :

For  $\text{Si}_{(g)}$ ,  $\Delta F_{3,000} = 10,618$  calorie/mole (Ref. 25, Stull and Sinke)  
using  $\text{Si}_{(1)}$  as reference state,

For  $\text{O}_{2(g)}$ ,  $\Delta F_{3,000} = 0$  (Since  $\text{O}_2$  is reference state),

For the formation of  $\text{SiO}_{(g)}$  (i.e., for the reaction  
 $\text{Si}_{(1)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{SiO}_{(g)}$ ),

$$\Delta F_{3,000} = \Delta H_{3,000} - T \Delta S_{3,000} = -38,954 - 3,000(\Delta S_{3,000}) \text{ calorie/mole}$$

$$\Delta S_{3,000} = S_{\text{SiO}} - \frac{1}{2}S_{\text{O}_{2(g)}} - S_{\text{Si}_{(1)}} = 10.17 \text{ e.u.}$$

and

$$\Delta F_{3,000} = 69,464 \text{ calorie/mole (for } \text{SiO}_{(g)} \text{ formation)}$$

where the entropies of  $\text{Si}_{(1)}$  and  $\text{O}_2$  are from Stull and Sinke<sup>25</sup> and that of  $\text{SiO}_{(g)}$  from our calculations. Assuming that  $\Delta H$  and  $\Delta S$  do not depend upon temperature, we find that  $\Delta F = -38,954 - 10.17 T$  for this reaction in the temperature range of  $2,000^\circ \text{K}$  to  $3,000^\circ \text{K}$ . From these data, we find that, for the first reaction given above, (i.e.  $\text{SiO}_{(g)} \rightarrow \text{Si}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$ )

$$\Delta F_{3,000} = + 80,082 \text{ calorie/mole}$$



and

$$\Delta S_{3,000} = \frac{1}{2} S_{O_{2(g)}} + S_{Si(g)} - S_{SiO(g)} = 16.31 \text{ e.u.}$$

Hence,  $\Delta F = 129,000 - 16.31T$  near  $T = 3,000^\circ K$ ,

Now we can calculate the equilibrium constant at  $3,000^\circ K$ ,

$$\begin{aligned} \Delta F_{3,000} &= -RT \ln K = 80,082 \\ \text{or } K &= 1.45 \times 10^{-6} = \frac{P_{SiPO_2}^{1/2}}{P_{SiO}} \end{aligned}$$

If we consider the case where  $P_{SiO} = 0.4 \text{ atm.}$  and  $P_{O_2} = 0.2 \text{ atm.}$ , (i.e., the approximate vapor pressures under neutral conditions at  $3,000^\circ K$  from figure 3) we find that

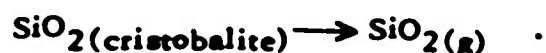
$$P_{Si} = 1.30 \times 10^{-6} \text{ atm.}$$

It can be seen that a negligible amount of monomeric  $Si(g)$  vapor exists under these conditions. Dimers and larger aggregates of Si would also be negligible under these conditions since the equilibrium studies of Honig<sup>24</sup> show the monomer to be the most important species, even when the condensed phase of silicon is present. The calculated partial pressure of silicon is far removed from such saturation conditions inasmuch as Stull and Sinke<sup>25</sup> report a boiling point of Silicon of  $2,950^\circ K$  and Honig<sup>37</sup> gives  $3,060^\circ K$ .

## VII. THERMOCHEMISTRY OF THE REACTION $\text{SiO}_{2(l)} \rightarrow \text{SiO}_{2(g)}$

### A. GENERAL

For estimation of thermochemical quantities involved in vaporization of liquid  $\text{SiO}_2$  to gaseous  $\text{SiO}_2$ , the most pertinent available data are those of Porter, Chupka, and Inghram.<sup>3</sup> They have made a mass spectrometric study of the decomposition of cristobalite at 1,800° K and 1,900° K.



They found that  $\Delta H_{298}^\circ = 136 \pm 8$  Kcalorie/mole, from slopes of their log  $\sum v_s 1/T$  data. However, in a personal communication Porter has stated that more accurate heat of reaction data (and hence free energy data) could be obtained for the above reaction with a suitable estimate of the entropy change in combination with their published pressures. Brewer and Searcy<sup>42</sup> have also discussed the value of this type of calculation.

### B. ESTIMATE OF ENTROPY FOR $\text{SiO}_{2(g)}$

Since there is little published information about  $\text{SiO}_{2(g)}$ , it has been necessary to make some assumptions about the configuration of the molecule. Knowledge about the  $\text{CO}_2$  molecule is used as the basis for estimating properties of the  $\text{SiO}_2$  molecule.

Since the  $\text{CO}_2$  molecule has a linear structure, it has been assumed that  $\text{SiO}_2$  is also linear. In estimating the interatomic distances the following data were considered:

<u>Molecule</u>	<u><math>r_e</math> (Å)</u>	<u>Ref.</u>
SiO	1.510	Herzberg <sup>32</sup>
CO	1.1284	Herzberg <sup>43</sup>
$\text{CO}_2$ ( $r_C = 0$ )	1.1615	Herzberg <sup>43</sup>

From these data we estimate the interatomic distance ( $\text{Si}-\text{O}$ ) of linear  $\text{SiO}_2$  to be 1.54Å.

The estimation of the vibrational frequencies for the linear  $\text{SiO}_2$  molecule has also been done by analogy with  $\text{CO}_2$ . In Table X are shown some

vibrational frequency data for  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{CO}$ , and  $\text{CS}$  molecules. It is seen that for the diatomic molecules the ratio of the vibrational frequencies,  $\nu_{\text{CS}}/\nu_{\text{CO}} = 0.59$  which agrees qualitatively (maximum error = 17 percent) with the corresponding ratios for the triatomic molecules  $\text{CO}_2$  and  $\text{CS}_2$ . The corresponding ratio of vibrational frequencies for the diatomic  $\text{SiO}$  and  $\text{CO}$  was obtained from Herzberg's book<sup>32</sup> which gives  $\nu_{\text{SiO}}/\nu_{\text{CO}} = 0.572$ . This ratio was then used to calculate the vibrational frequencies of  $\text{SiO}_2$  from the corresponding frequencies for  $\text{CO}_2$ . This calculation is approximate and the calculated vibrational frequencies might be in error by as much as 15 to 20 percent.

TABLE X

VIBRATIONAL FREQUENCY DATA ESTIMATED FOR  $\text{SiO}_2(\text{g})$

<u>Mode</u>	<u><math>\text{CO}_2</math></u>	<u><math>\text{CS}_2</math></u>	<u>Ratio <math>\nu_{\text{CS}_2}/\nu_{\text{CO}_2}</math></u>	<u>Ref.</u>
Stretching, $\nu_1$	1,342 $\text{cm}^{-1}$	656.5	0.49	Herzberg <sup>43</sup>
Bending, $\nu_2$ (degenerate)	667	396	0.59	Herzberg <sup>43</sup>
Stretching, $\nu_3$	2,349	1,523	0.65	Herzberg <sup>43</sup>
	<u><math>\text{CO}</math></u>	<u><math>\text{CS}</math></u>	<u>Ratio <math>\nu_{\text{CS}}/\nu_{\text{CO}}</math></u>	
$\nu_1$	2,170	1,285	0.59	Herzberg <sup>32</sup>
	<u><math>\text{CO}</math></u>	<u><math>\text{SiO}</math></u>	<u>Ratio <math>\nu_{\text{SiO}}/\nu_{\text{CO}}</math></u>	
$\nu_1$	2,170	1,242	0.572	Herzberg <sup>32</sup>
	<u><math>\text{CO}_2</math></u>	<u><math>\text{SiO}_2</math> (calculated)</u>	<u>Ratio <math>\nu_{\text{SiO}_2}/\nu_{\text{CO}_2}</math> (assumed)</u>	
$\nu_1$	1,342 $\text{cm}^{-1}$	767	0.572	
$\nu_2$	667	382	0.572	
$\nu_3$	2,349	1,340	0.572	

For the moment of inertia of the  $\text{SiO}_2$  molecule, we used the relation given by Herzberg<sup>43</sup> for the moment of inertia of a symmetrical molecule.

$$I_B = 2M_O r_{\text{Si}-O}^2$$

where  $M_O$  is the mass of the oxygen atom and  $r_{\text{Si}-O}$  is the interatomic distance

$$M_O = 16 \times 1.66 \times 10^{-24} \text{ gm}$$

$$r_{\text{Si}-O} = 1.54 \text{ \AA} = 1.54 \times 10^{-8} \text{ cm},$$

Hence, we estimate for  $\text{SiO}_2$  that

$$I_B = 1.26 \times 10^{-38} \text{ gm-cm}^2$$

For the temperature ranges of possible interest in this calculation ( $T < 5,000^\circ \text{ K}$ ), electronic contributions are assumed to be negligible. It is assumed that only a single electronic ground state is occupied because the  $\text{SiO}_2$  molecule has an even number of electrons. Dr. Beckett, of the National Bureau of Standards in a private communication has stated that very roughly speaking the  $n$  higher state would probably be at least 5 e.v. above the ground state. Since 5 e.v. corresponds to a value of  $RT = 115,300$  calorie, or  $T = 58,000^\circ \text{ K}$ , it can be seen that contributions to the partition function will be negligible at the temperatures under consideration here and essentially only the ground electronic state will be occupied.

The calculation of the entropy for  $\text{SiO}_2(g)$  was made with the statistical mechanical formula given by Kelley<sup>14</sup> for linear polyatomic molecules.

$$S = 3/2 R \ln_e M + 7/2 R \ln_e T - R \ln P + R \ln I - R \ln \sigma - + \sum S(\text{Einstein}) + S_{el}^0 + 175.385$$

The present calculation is for atmosphere pressure and so the third term above does not contribute to  $S$ . The symmetry number  $\sigma$  has the value two for the  $\text{SiO}_2$  molecule. Evaluation of the  $\sum S(\text{Einstein})$  contribution must be

made for the four vibrational degrees of freedom for a linear triatomic molecule.

Terms for  $\nu_1$  and  $\nu_3$  contribute once each to this sum whereas those for  $\nu_2$  (the bending vibration) contribute twice. The tables of Taylor and Glasstone<sup>44</sup> have facilitated evaluation of the vibrational terms. No attempt has been made to incorporate refinements such as Fermi resonance which apply to the  $\text{CO}_2$  molecule.

Enthalpy calculations were made with the relation

$$\frac{(H - H_0)}{T} = \frac{7}{2} R = 6.954$$

Translation + rotation + el

The terms due to vibration can again be added from Taylor and Glasstone's<sup>44</sup> tables.

In Table XI are listed the resulting heat capacity, enthalpy, and entropy data calculated for the linear  $\text{SiO}_2(\text{g})$  molecule.

**TABLE XI**  
HEAT CAPACITY, ENTHALPY, AND ENTROPY DATA

FOR THE ASSUMED, LINEAR $\text{SiO}_2(\text{g})$ MOLECULE					
Temper- ature ( $^{\circ}\text{K}$ )	$C_p$ (calorie/ mole $^{\circ}\text{K}$ )	$\frac{(H-H_0)}{T}$ (calorie/ mole $^{\circ}\text{K}$ )	$H-H_0$ (calorie/ mole)	$H-H_{298}$ (calorie/ mole)	$S$ (e. u.)
298	10.80	8.53	2,542	0	54.65
500	12.55	9.83	4,915	2,373	
1,000	14.10	11.66	11,660	9,118	
1,500	14.50	12.57	18,855	16,313	
1,800		12.90	23,220	20,678	78.57
1,900		12.99	24,681	22,139	79.37
2,000	14.67	13.06	26,120	23,578	80.06
2,500	14.73	13.40	33,500	30,958	83.37
3,000	14.79	13.62	40,860	38,318	85.96

The heat capacity data obtained in Table XI are plotted in figure 8. For comparison purposes the heat capacity of  $\text{CO}_2(\text{g})$  has been included. It is seen that above  $2,500^\circ \text{K}$  the heat capacity of  $\text{CO}_2$  exceeds the estimated heat capacity for  $\text{SiO}_2(\text{g})$ . This probably occurs because such complicating factors in  $\text{CO}_2$  as the Fermi resonance (or accidental degeneracy) and other refinements have not been considered in the present calculation.

From Porter et al's paper <sup>3</sup>, we obtain for the reaction  $\text{SiO}_2(\text{crist}) \rightarrow \text{SiO}_2(\text{g})$  the vapor pressure data shown in Table XII. The free energies shown were calculated from their vapor pressure data.

TABLE XII

DATA FOR  $\text{SiO}_2(\text{crist}) \rightarrow \text{SiO}_2(\text{g})$

	<u>1,800° K</u>	<u>1,900° K</u>
$P_{\text{SiO}_2}$ (atm.)	$1.6 \times 10^{-8}$	$1.0 \times 10^{-7}$
$\Delta F = -RT \ln P_{\text{SiO}_2}$ (calorie/mole)	+64,214	+60,860
$S_{\text{SiO}_2(\text{g})}$ (from Table XI) e. u.	78.57	79.37
$S_{\text{SiO}_2(\text{crist})}$ (from Kelley <sup>1,9</sup> ) e. u.	38.15	39.12
$\Delta S$ e. u.	40.42	40.25
$T \Delta S$ calorie/mole	72,756	76,475
$\Delta H_T = \Delta F + T \Delta S$ calorie/mole	136,970	137,335

To convert the heat of reaction data at 1,800° and 1,900° K to heat of reaction data at 298° K, we can use the values from Table XI for the heat content of  $\text{SiO}_2(\text{g})$  and those from Kelley<sup>13</sup> for that of cristobalite at 1,800° K. In this way, one obtains

$$\Delta H_{298} = \Delta H_T - (H_T - H_{298})_{\text{SiO}_2(\text{g})} + (H_T - H_{298})_{\text{SiO}_2(\text{crist})}$$

$$\Delta H_{298} = 140,822 \text{ calorie/mole}$$

Also, from data at 1,900° K, we obtain

$$\Delta H_{298} = 141,516 .$$

The average of these two results is  $\Delta H_{298} = 141,169$  calorie/mole. This value is somewhat higher than the original value reported by Porter et al of  $136,000 \pm 8,000$  calorie/mole but falls within their range of uncertainty.

$\Delta H_{2,000}$  for the reaction  $\text{SiO}_2(\text{crist}) \rightarrow \text{SiO}_2(\text{g})$ , is calculated as follows:

$$\Delta H_{2,000} = \Delta H_{298} + (H_T - H_{298})_{\text{SiO}_2(\text{g})} - (H_T - H_{298})_{\text{crist.}}$$

$$\Delta H_{2,000} = 136,627 \text{ calorie/mole}$$

By taking into account the heat of fusion of cristobalite (2,500 calorie/mole), we can calculate the heat of vaporization of liquid silica

$$\text{SiO}_2(\text{l}) \rightarrow \text{SiO}_2(\text{g}) \quad \Delta H_{2,000} = 134,127 \text{ calorie/mole}$$

from the above.

For the heat of this reaction at higher temperatures we have

$$\Delta H_T = \Delta H_{2,000} + (H_T - H_{2,000})_{\text{SiO}_2(g)} - (H_T - H_{2,000})_{\text{SiO}_2(l)} .$$

The additional necessary data for calculations of  $\Delta H_T$  are in Table I and Table XI. Results of such a calculation are summarized in Table XIII.

TABLE XIII  
HEAT OF VAPORIZATION OF LIQUID  $\text{SiO}_2$

	$\text{SiO}_2(l) \rightarrow \text{SiO}_2(g)$		
	<u>2,000° K</u>	<u>2,500° K</u>	<u>3,000° K</u>
$(H_T - H_{2,000})_{\text{SiO}_2(l)}$ (calorie/mole)	0	10,830	21,660
$(H_T - H_{2,000})_{\text{SiO}_2(g)}$ (calorie/mole)	0	7,380	14,740
$\Delta H$ (calorie/mole)	134,127	130,677	127,207

Likewise, to calculate the entropy change for the last reaction, the data of Table VI and Table XI can be used as shown in Table XIV.

The free energy data given in Table XIV, have been plotted in figure 1, where it can be seen that  $\Delta F = 0$  ( $P_{\text{SiO}_2} = 1 \text{ atm.}$ ) at  $T = 3,540^\circ \text{ K}$ . These data show that at  $3,000^\circ \text{ K}$ ,  $\Delta F = 19,416$  calorie/mole and

$$P_{\text{SiO}_2} = e^{\frac{-19,416}{R \times 3,000}} = 0.039 \text{ atm.}$$



**TABLE XIV**

**ENTROPY CHANGE FOR VAPORIZATION OF LIQUID SiO<sub>2</sub>**

		$\text{SiO}_2(1) \rightarrow \text{SiO}_2(g)$		
		<u>2,000° K</u>	<u>2,500° K</u>	<u>3,000° K</u>
$S_{\text{SiO}_2(g)}$	(e. u.)	80.06	83.37	85.96
$S_{\text{SiO}_2(1)}$	(e. u.)	41.07 ± 0.6	46.13 ± 0.8	50.03 ± 1.0
$\Delta S$	(e. u.)	38.99	37.24	35.93
$T\Delta S$	(calorie/mole)	77,980	93,100	107,791
$\Delta H$	(calorie/mole)	134,127	130,677	127,207
$\Delta F = \Delta H - T\Delta S$	(calorie/mole)	56,147	37,577	19,416

SiO<sub>2(g)</sub> pressures as a function of 1/T are shown in figures 2 and 11. In this case the equilibrium constant is equal to the partial pressure of SiO<sub>2(g)</sub> in atmospheres. If SiO<sub>2</sub> vaporizes according to the above reaction at 3,000° F, then the total amount of heat absorbed, including the sensible heat of solid and liquid SiO<sub>2</sub> from 298° to 3,000° K, is

$$\begin{aligned} \Delta H_{\text{total}}_{3,000^\circ\text{K}} &= (H_{3,000} - H_{298})_{\text{SiO}_2(1)} - \Delta H_{\text{vaporization}}_{3,000^\circ\text{K}} \\ &= (H_{2,000} - H_{298})_{\text{SiO}_2(\text{glass})} + (H_{3,000} - H_{2,000})_{\text{SiO}_2(1)} + \Delta H_{\text{vaporization}} \end{aligned}$$

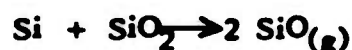
$$\Delta H_{\text{total}}_{3,000^\circ\text{K}} = 177,877 \text{ calorie/mole (5,336 Btu/lb).}$$

The sensible heat (the first two terms in the second equation) contributes 50,670 calorie/mole (1,520 Btu/lb.), and the vaporization contributes 127,207 calorie/mole (3,816 Btu/lb). It should be noted that simple vaporization of  $\text{SiO}_2(\text{g})$  at 3,000° K gives a total heat absorption of only 5,336 Btu/lb as against the value of 6,650 Btu/lb found for the case of  $\text{SiO}(\text{g})$  and  $\text{O}_2(\text{g})$  formation.

## VIII. $\text{SiO}_2$ IN REDUCING ATMOSPHERES

In a reducing atmosphere decomposition of  $\text{SiO}_2$ , to produce  $\text{SiO}_{(g)}$ , occurs at a much lower temperature than under neutral or oxidizing conditions. Three typical reducing agents, for which data are available, include elemental silicon, carbon, and hydrogen. Since the reducing reactions occur at lower temperatures they are of possible interest for at least two important reasons. First, a re-entry vehicle might be constructed out of a mixture of  $\text{SiO}_2$  and a reducing agent. This might permit decomposition of  $\text{SiO}_2$  to occur at a lower temperature where its viscosity is still high. Second, knowledge of the effect of reducing reactions is important because many of the current testing procedures in arcs are being carried out under reducing conditions. That is, arc testing done with carbon electrodes which yield carbon atoms in the plasma may really correspond to a reducing atmosphere when carbon is present in excess of oxygen or if the other ingredients of the plasma are present in stoichiometric amounts of reducing and oxidizing agents. Also, if a test specimen in the arc is subject to stoichiometric amounts of H atoms and OH atoms (reducing agent and oxidizing agent respectively), the higher mobility of the H atoms may effectively make the specimen "see" a reducing atmosphere.

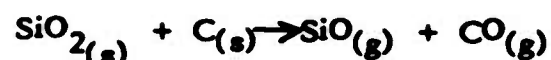
The reaction between stoichiometric amounts of silicon and silica leads to the reaction:



Although  $\text{Si} + \text{SiO}_2$  in a closed system will decompose at a lower temperature than either material separately, it cannot be concluded that the reaction is independent of oxygen pressure. This arises from the fact that the simultaneous reaction  $\text{Si} + \text{O}_2$  must be considered. In the dynamic case involving decomposition of the re-entry vehicle surface, it is possible and, very likely, that the reaction  $\text{Si} + \text{SiO}_2$  will be the most important. However, if one is discussing an equilibrium case where an unlimited amount of oxygen is available, then the process reverts to a decomposition of  $\text{SiO}_2$  in an oxidizing atmosphere.

Some typical vapor pressure data for the Si-SiO<sub>2</sub> reaction taken from Humphrey, Todd, Coughlin, and King<sup>18</sup> are plotted in the lower curve of figure 9.

For the reducing reaction between carbon and silica, one of the possible reactions is that for the formation of  $\text{SiO}_{(g)}$  and  $\text{CO}_{(g)}$ .



The data for this reaction were taken from Humphrey's tables<sup>18</sup> and plotted in figure 9. The upper curve gives the CO pressure while the lower curve is again assumed to represent the actual SiO pressure in the system because of disproportionation to  $\text{Si}_{(s)}$  and  $\text{SiO}_{2(s)}$ . Reference to these data would indicate that a pressure of one atm (  $P_{\text{CO}} = 0.89$  atm,  $P_{\text{SiO}} = 0.11$  atm ) is reached at a temperature of 1,845° K. The assumption that the SiO pressure is fixed by the Si-SiO<sub>2</sub> equilibrium appears to be quite valid since if it had been ignored higher SiO pressures would have been obtained by calculation. Of course, the  $\text{SiO}_{(s)} = \text{SiO}_{(g)}$  equilibrium instead of the Si-SiO<sub>2</sub> equilibrium may fix the  $\text{SiO}_{(g)}$  pressure in the present case. Actually these two equilibria are probably quite similar (i. e. , give the same  $\text{SiO}_{(g)}$  pressure at temperatures near 1,700° to 1,800° K) if we assume, as discussed in section II, that  $\text{SiO}_{(s)}$  becomes stable near 1,450° to 1,573° K.

Another reducing reaction of interest is that of SiO<sub>2</sub> with H<sub>2</sub>. The applicable experimental data of Grube and Speidel<sup>21</sup>, as given by Edwards<sup>19</sup>, have been plotted in figure 10. Here, it can be seen that their tabulated vapor pressure data for  $\text{SiO}_{(g)}$  are in agreement with those determined by Tombs and Welch<sup>23</sup>. Figure 10 also shows expected vapor pressures of  $\text{SiO}_{(g)}$  corresponding to the vaporization of  $\text{SiO}_{(s)}$  or  $\text{Si}_{(-)} + \text{SiO}_{2(s)}$ . It should be noted that in an H<sub>2</sub> atmosphere the pressure of  $\text{SiO}_{(g)}$  is less than either of these equilibria would predict and hence SiO gas will be formed rather than a solid phase. These results show that decomposition of SiO<sub>2</sub> under these conditions occurs at much lower temperatures than under oxidizing or neutral conditions.

# IX. SUMMARY OF CALCULATED VAPORIZATION DATA FOR $\text{SiO}_2(1)$ AND COMPARISON WITH PUBLISHED VALUES

In the preceding sections various equilibria, involving  $\text{SiO}_2$ , have been considered. The data show that the first reaction,  $\text{SiO}_2(1) \rightarrow \text{SiO}(g) + \frac{1}{2} \text{O}_2(g)$ , is most important for neutral conditions. However, the reaction  $\text{SiO}_2(1) \rightarrow \text{SiO}_2(g)$ , makes a significant contribution to the vapor pressure. It becomes even more important under oxidizing conditions.

For each of the reactions considered, a standard free energy of reaction has been obtained. Simple approximate formulas have been developed to express these free energies as functions of temperature. The resulting formulas are summarized in Table XV. From these approximate relations or the somewhat more accurate data obtained earlier in this paper for a few of the reactions, equilibrium constants have been calculated by means of the relation

$$K = e^{-\Delta F^\circ/RT} . \quad \text{The results are plotted in figure 2.}$$

Although vaporization phenomena were discussed in terms of the single reaction,  $\text{SiO}_2 \rightarrow \text{SiO}(g) + \frac{1}{2} \text{O}_2(g)$ , it is now possible to consider an additional reaction, the dissociation of oxygen. The effect of the latter can be evaluated both for the case of neutral conditions and for the case of oxidizing conditions.

## A. NEUTRAL CONDITIONS

For the case of neutral conditions we start with the reactions



and let

$P_{\text{SiO}}$  = partial pressure of  $\text{SiO}$ ,

$P_{\text{O}_2}$  = partial pressure of  $\text{O}_2$ ,

TABLE XV

## FREE ENERGY RELATIONS FOR VARIOUS REACTIONS

Reaction	Free Energy Change, calories/mole	Estimated Uncertainty calories/mole	Temperature Range, °K	Remarks and Sources of Data
$\text{SiO}_{2(\text{cris})} \longrightarrow \text{SiO}_{(\text{g})} + 1/2\text{O}_{2(\text{g})}$	$\Delta F^\circ = 180,800 - 58.11T$	$\pm 3000$	1800 - 2000	Data based on Schafer and Hornle
$\text{SiO}_{2(\text{l})} \longrightarrow \text{SiO}_{(\text{g})} + 1/2\text{O}_{2(\text{g})}$	$\Delta F^\circ = 173,000 - 54.2T$	$\pm 4000$	2000 - 4000	
$\text{SiO}_{(\text{s})} \longrightarrow \text{SiO}_{(\text{g})}$	$\Delta F^\circ = 77,530 - 34.9T$	$\pm 8000$	1800 - 2000	May be used at higher temperatures; Melting point of $\text{SiO}_{(\text{s})}$ is unknown. Uncertainty is a guess.
$\text{Si}_2\text{O}_{2(\text{g})} \longrightarrow 2\text{SiO}_{(\text{g})}$	$\Delta F^\circ = +52,500 - 33.4T$	$\pm 10,000$	1500 - 3000	Data based on Porter et al.
$1/2\text{O}_{2(\text{g})} \longrightarrow \text{O}_{(\text{g})}$	$\Delta F^\circ = 61,348 - 16.11T$	$\pm 400$	2000 - 4000	For tabulated data, see Stull and Sinke. <sup>25</sup> ( $\Delta H_{\text{O}}^\circ = 58,980$ ) or older NBS tables ( $\Delta H_{\text{O}}^\circ = 58,586$ ).
$\text{SiO}_{2(\text{l})} \longrightarrow \text{SiO}_{2(\text{g})}$	$\Delta F^\circ = 127,200 - 36.0T$	$\pm 6000$	2000 - 4000	Data based on Porter et al.
$\text{Si}_{(\text{l})} + \text{O}_{2(\text{g})} \longrightarrow \text{SiO}_{(\text{g})}$	$\Delta F^\circ = -38,954 - 10.17T$	$\pm 3000$	1700 - 2950	
$\text{SiO}_{(\text{g})} \longrightarrow \text{Si}_{(\text{g})} + 1/2\text{O}_{2(\text{g})}$	$\Delta F^\circ = 129,000 - 16.31T$	$\pm 3000$	near 3000	

$P_O$  = partial pressure of O.

Under our assumed conditions, we have the additional relations

$$P_{O_2} + \frac{1}{2}P_O = \frac{1}{2}P_{SiO} \quad (10)$$

$$K_1 = P_{SiO} \cdot P_{O_2}^{\frac{1}{2}}, \quad (11)$$

and

$$K_2 = \frac{P_O}{P_{O_2}^{\frac{1}{2}}} \quad (12)$$

The above three equations are sufficient to determine the three unknowns in terms of the two equilibrium constants,  $P_{SiO}$ ,  $P_{O_2}$ , and  $P_O$ .

Rearranging equation (12) to

$$P_O = K_2 P_{O_2}^{\frac{1}{2}} \quad (13)$$

and substituting into equation (10), we obtain,

$$2 P_{O_2} + K_2 P_{O_2}^{\frac{1}{2}} = P_{SiO} \quad (14)$$

Finally, we substitute (14) into (11) and obtain the cubic equation,

$$2 P_{O_2}^{3/2} + K_2 P_{O_2} - K_1 = 0 \quad (15)$$

for  $P_{O_2}$  in terms of  $K_1$  and  $K_2$ .

For the case where  $K_2$  is small, i.e., where the dissociation of  $O_2$  is negligible, we can solve equation (15) readily to obtain

$$P_{O_2} \approx (K_1/2)^{2/3} \quad (K_1 \ll K_2 P_{O_2}) \quad (16)$$

For the case where we cannot neglect dissociation of  $O_2$ , equation (15) must be solved.

After solving equation (15) for  $P_{O_2}$  we can obtain  $P_O$  from equation (13) and  $P_{SiO}$  from equation (10).

From selected values of the equilibrium constants  $K_1$  and  $K_2$  at  $2,000^\circ$ ;  $2,500^\circ$ ,  $3,000^\circ$ ,  $3,500^\circ$ , and  $3,750^\circ$  K, it has been possible to calculate corresponding values of the partial pressures of SiO,  $O_2$ , and O as described above. The resulting calculated partial pressures, based on neutral conditions and including dissociation of oxygen, have been plotted in figure 11.

Referring to the data in figure 11, one can see that a total pressure of one atmosphere is obtained at  $3,070^\circ$  K. This corresponds to the normal boiling point of  $SiO_2$ . By reading partial pressures of the various components from the graph at  $3,070^\circ$  K, one obtains the following:

$$\begin{array}{ll} P_{SiO} = 0.62 \text{ atm} & ( + 0.6 \text{ or } - 0.2 ), \\ P_{O_2} = 0.26 \text{ atm} & ( + 0.25 \text{ or } - 0.08 ), \\ P_O = 0.074 \text{ atm} & ( + 0.07 \text{ or } - 0.002 ), \\ P_{SiO_2} = 0.058 \text{ atm} & ( + 0.12 \text{ or } - 0.002 ), \\ \underline{P_{Si_2O_2} = 0.0001 \text{ atm}} & ( + 0.0003 \text{ or } - 0.00003 ), \\ P_{total} = 1.012 & ( + 1.04 \text{ atm or } - 0.28 \text{ atm} ) \end{array}$$

The uncertainties in the partial pressures are indicated in parentheses. For example,  $P_{SiO}$  may possibly have values from 0.42 to 1.22 at  $3,070^\circ$  K.

It is seen that within the accuracy of these data, a total pressure of one atmosphere is obtained at  $3,070^\circ \pm 75^\circ$  K for a neutral equilibrium mixture. The accuracy of this boiling point can be determined from the fact that the free energy function of importance here is

$$\Delta F^\circ = 173,000 - 54.2 T$$

where



$\Delta F^\circ$  is accurate to  $\pm 4,000$  calories/mole near  $3,000^\circ \text{K}$ .

Using this uncertainty in  $\Delta F^\circ$  we obtain  $\frac{d(\Delta F^\circ)}{dT} = 54.2$ , from which it follows that  $\Delta T = \pm 75^\circ \text{K}$ .

A more complete analysis of the expected equilibrium gaseous species at  $3,000^\circ \text{K}$  is as follows:

<u>Species</u>	<u>Pressure (atm)</u>
SiO	0.43
SiO <sub>2</sub>	0.04
Si <sub>2</sub> O <sub>2</sub>	$5 \times 10^{-5}$
(SiO) <sub>x</sub>	unknown
O <sub>2</sub>	0.18
O	0.05
Si	<u><math>1.3 \times 10^{-6}</math></u>
P <sub>total</sub>	0.70 atm

The results summarized in both of the above tables show that SiO and O<sub>2</sub> are the predominant species. In the neutral, equilibrium mixture Si and Si<sub>2</sub>O<sub>2</sub> are present in minor amounts. However, significant amounts of SiO<sub>2</sub> and O are also present.

As we have just seen, a normal boiling point of  $3,070^\circ \text{K}$  is predicted for SiO<sub>2</sub>. If all the other reactions had been neglected and only the decomposition reaction  $\text{SiO}_2 \rightarrow \text{SiO(g)} + \frac{1}{2}\text{O}_2(\text{g})$  had been considered, then a boiling point of  $3,085^\circ \text{K}$  would have been predicted, as discussed earlier. Thus, the other reactions have only a small effect on the predicted boiling point. The possibility of reactions, other than those already discussed, should not be completely overlooked, but they are not likely to be important. In the absence of further information and in view of the fact that the observed reactions predict vaporization phenomena in agreement with experiments at lower temperatures, it does seem likely that the present calculations should give a fair figure for the boiling point.

Table XVI contains values of boiling points given in the literature which can be compared with ours.

TABLE XVI  
TABULATED BOILING POINTS FOR SiO<sub>2</sub>

<u>Temperature</u>	<u>Original Reference</u>	<u>Date</u>	<u>Quoted by</u>
2,230° C	Ruff and Schmidt <sup>4</sup>	1921	(Lange <sup>45</sup> -Handbook of Chemistry) (Handbook of Chemistry and Physics <sup>46</sup> ) (Int. Critical Tables <sup>47</sup> )
2,590° C	Ruff and Konschak <sup>5</sup>	1926	(Handbook of Chemistry and Physics <sup>46</sup> ) (Sidgwick <sup>48</sup> , Eitel <sup>49</sup> )
2,800° C	Present work		
2,950° C	O. Ruff <sup>6</sup>	1935	(A. Silverman <sup>50</sup> ) (Campbell <sup>11</sup> )
3,500° C	W. R. Mott <sup>51</sup>	1918	

In reviewing the above data it was found that Brewer<sup>39</sup> has rightfully criticized the boiling point data of Ruff and Schmidt<sup>4</sup> because the measurements were carried out in a carbon vapor (reducing) atmosphere. The original paper by Ruff and Konschak<sup>5</sup> also shows uncertainty of the same type. Although they used an iridium container, it was inside a graphite vessel. Under such conditions they observed rapid attack of the iridium container and were able to obtain only a single measurement at 2,060° C. They used this measurement to obtain their extrapolated boiling point. In view of the fact that their container was subject to such rapid attack, it appears possible that a reducing atmosphere (of iridium or carbon) was actually present. This would lead to observation of a higher vapor pressure and, hence, a lower boiling point than the true one. Other container materials tried by Ruff and Konschak<sup>5</sup> without success included tantalum, tungsten, molybdenum, and zirconium oxide. Ruff and Konschak<sup>5</sup> further state that their calculated boiling point of 2,590° C is only a minimum value.

The boiling point of 2,950° C given by Ruff<sup>6</sup> in 1935 was simply a restatement of his earlier work of 1926. In 1935 he stated that the original 2,590° C boiling point was a misprint and that the measured 11.0 mm pressure at 2,060° C should extrapolate to a boiling point of 2,950° C. However, in repeating his extrapolation we find that the 2,590° C boiling point appears more reasonable. In figure 12, for example, the extrapolation through the ordinate 11.1 at  $\frac{1}{T} = 0$ , as recommended by Ruff in 1926 leads to  $\log_{10} 760 \text{ mm} = 2.88$  at 2,590° C as he had reported at that time.

If we plot the three calculated vapor pressure figures as given by Ruff in 1935 and draw the dashed line shown in the graph (figure 12), we obtain an intercept of 8.15 at  $1/T = 0$ .

Since

$$P_{\text{mm}} = P_{\text{atm}} \times 760$$

and

$$\log_{10} P_{\text{mm}} = \log_{10} P_{\text{atm}} + \log_{10} 760 ,$$

the intercepts for the different pressure units are therefore

$$\left[ \log_{10} P_{\text{mm}} \right]_{1/T = 0} = 11.03$$

$$\left[ \log_{10} P_{\text{atm}} \right]_{1/T = 0} = 8.15$$

A value of 8.15 for the intercept at  $1/T = 0$  would appear reasonable if the ordinate were given as  $\log_{10} P_{\text{atm}}$  instead of the  $\log_{10} P_{\text{mm}}$  actually used.

It thus appears that Ruff may have mistakenly used 8.15 as an intercept when  $\log_{10} P_{\text{mm}}$  was plotted as the ordinate. Actually, to be correct, it is necessary to plot  $\log_{10} P_{\text{atm}}$  in conjunction with the 8.15 intercept.

In view of the uncertainties in the analysis just given above, it is desirable to present some independent data supporting Ruff's 1926 extrapolation to an intercept of 11.1 at  $1/T = 0$ . We have already shown in Section II, E that

$$P_t(\text{atm}) = 3/2 e^{18.41 (1 - \frac{3160}{T})}$$

or

$$P_t(\text{mm}) = 3/2 \times 760 e^{18.41 (1 - \frac{3160}{T})}$$

The second equation can be rearranged to the form

$$\log_{10} P_t(\text{mm}) = 11.1 - 25,200/T$$

in which it is obvious that the intercept is 11.1.

We therefore conclude that the boiling point of 2,950° C given by Ruff in 1935 is too high. On the other hand the value of 2,590° C is only a lower limit. This is particularly true since his measurements were performed under reducing conditions.

Information on the very high boiling point of 3,500° C given by Mott<sup>51</sup> in 1918 indicates that this measurement was a very rough one. SiO<sub>2</sub> was decomposed in an arc, and the temperature measurements were necessarily quite uncertain.

Summarizing then, the recorded boiling points for SiO<sub>2</sub>, in the literature, are spread over a considerable range. The lower values of 2,230° C and 2,590° C must be considered as lower limits. The value of 2,950° C is apparently a mistake and the value of 3,500° C is only an approximation. Thus, our calculated value of 2,800° C appears to be reasonable and is probably more reliable than the values in the literature.

Additional vapor pressure data for the decomposition of SiO<sub>2</sub>, under so-called neutral conditions, have been given by Brewer and Mastick<sup>2</sup>, Inuzuka and Ageha<sup>38</sup>, and Porter, Chupka, and Inghram<sup>3</sup>. The data of Brewer and Mastick have been shown to agree with the calculations based on the first reaction  $\text{SiO}_2 \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ . Inasmuch as we have found that consideration of all the other possible reactions only changed the predicted boiling point from 3,085° K to 3,070° K, it can be seen that the first reaction is of primary importance. Our calculated vapor pressure data at low temperatures

are compared with the data of Brewer and Mastick<sup>2</sup> in figure 5. The agreement is good and, if anything, Brewer and Mastick's<sup>2</sup> extrapolated data might indicate an even higher boiling point than the one we have calculated.

The data of Porter et al<sup>3</sup> are seen to be too high relative to our vapor pressures in figure 5. However, they were apparently not operating under strictly neutral conditions. Thus, for 1,900° K they gave  $p_{\text{SiO}} = 3.4 \times 10^{-5}$  and  $p_{\text{O}_2} = 8.2 \times 10^{-8}$  atm. It follows that  $p_{\text{SiO}} p_{\text{O}_2}^{1/2} = 9.7 \times 10^{-9}$  atm <sup>3/2</sup>,

and that

$$\Delta F_{\text{Porter, 1,900}} = + 69,595 \text{ calorie/mole}$$

As seen in Table VII-A, this free energy value agrees closely with our thermochemical value of 71,000 calories/mole.

The data of Inuzuka and Ageha<sup>38</sup> were discussed earlier and it was shown that their reported high vapor pressure data could be accounted for by a reducing reaction involving the molybdenum wire. In fact, the excellent agreement obtained with the thermochemical data for  $\text{SiO}_{(g)}$  suggests that these data are fairly reliable.

## B. OXIDIZING CONDITIONS

Just as in the case of neutral conditions we consider the same two reactions for the case of oxidizing conditions in air. That is, we neglect other possible reactions. It is possible that excess oxygen or nitrogen might lead to new species which are not considered, here, but until experimental data clarify this point we make the assumption that other reactions are negligible.



It is assumed that  $\text{SiO}_2$  decomposes in the presence of air at various total pressures,  $p_t$ . For the present case, nitrogen is assumed to be inert. Then we have the following relations:

$$P_t = P_{N_2} + P_{O_2} + P_{SiO} + P_O, \quad (19)$$

$$P_{N_2} = 4(P_{O_2} + \frac{1}{2}P_O - \frac{1}{2}P_{SiO}), \quad (20)$$

$$K_1 = P_{SiO} P_{O_2}^{\frac{1}{2}}, \quad (21)$$

$$K_2 = P_O / P_{O_2}^{\frac{1}{2}}, \quad (22)$$

We can solve the above set of four equations for the four unknowns  $P_{N_2}$ ,  $P_{O_2}$ ,  $P_O$ , and  $P_{SiO}$  in terms of  $P_t$ ,  $K_1$ , and  $K_2$  as known parameters. Combining equations (19) and (20) we get

$$P_t = 5 P_{O_2} + 3 P_O - P_{SiO}, \quad (23)$$

But from equation (22),  $P_O = K_2 P_{O_2}^{\frac{1}{2}}$ , and equation (23) becomes

$$P_t = 5 P_{O_2} + 3 K_2 P_{O_2}^{\frac{1}{2}} - P_{SiO} \quad (24)$$

or

$$P_{SiO} = 5 P_{O_2} + 3 K_2 P_{O_2}^{\frac{1}{2}} - P_t. \quad (25)$$

Also from equation (21) we have

$$P_{SiO} = \frac{K_1}{P_{O_2}^{\frac{1}{2}}} \quad (26)$$

Combining this with equation (25), we finally get

$$5 P_{O_2}^{\frac{3}{2}} + 3 K_2 P_{O_2} - P_t P_{O_2}^{\frac{1}{2}} - K_1 = 0 \quad (27)$$

After this cubic equation has been solved for  $p_{O_2}$ , the other unknowns can be evaluated from equations (26), (22) and (20).

Solutions for this set of equations were obtained for values of  $p_t = 0.1, 1, 10,$  and  $50$  atm. Calculations were made in the range of  $2,000^\circ$  to  $3,750^\circ$  K. The resulting data have been plotted in figures 13, 14, 15, and 16 which show the partial pressures of SiO,  $O_2$ ,  $SiO_2$ , and  $N_2$  as functions of  $1/T$ .

It is seen that at temperatures well below the boiling point, the  $SiO_{(g)}$  formation is markedly repressed. Thus from figure 13 at  $p_t = 0.1$  atm and  $T = 2,000^\circ$  K, the SiO partial pressure is essentially equal to the  $SiO_2$  partial pressure. However, in this case a boiling point is not reached until about  $2,700^\circ$  K. At all higher temperatures,  $SiO_{(g)}$  formation becomes more important than  $SiO_{2(g)}$  formation. For reference purposes in figures 13 through 16, the vaporization curve for SiO under neutral conditions is also given. The curves given in each of the figures extend up to the boiling point. At higher temperatures, total pressures are obtained in excess of the postulated pressure. At the boiling point and higher temperatures the  $N_2$  pressure is zero. Also at the higher temperatures, the SiO,  $O_2$  and O partial pressures are the same as for the neutral conditions already discussed. However, these data are not repeated in figures 13 through 16. The rapid variation in partial pressure of  $N_2$  has not been indicated with much precision but an approximate indication is given in the figures.

The data presented in figures 13 through 16 show that under some conditions the oxygen present in air is sufficient to repress SiO formation significantly. Although the effect decreases near the boiling point it becomes very pronounced at lower temperatures.

Consequently, in any proposed application of fused silica, the conditions of the high-temperature exposure must be known before the equilibrium gas species can be estimated.

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## XI. ACKNOWLEDGMENTS

The author wishes to thank Dr. W. Bade who offered numerous helpful suggestions during the present study. Dr. M. S. Klamkin and the Mathematics Section solved the cubic equation listed in the text. Drs. R. Barriault and M. Malin provided helpful guidance. Several people participated in discussions of the topics covered including Drs. B. Kivel, M. Panish, and S. Ruby.

## APPENDIX A

### SUMMARY OF PHYSICAL AND CHEMICAL PROPERTIES OF SILICA

Because of the great current interest in silica as a possible consumable re-entry vehicle material, there is a need for a convenient summary of the best available data on its properties. The following summary presents these data in a concise systematic form. It contains not only the material from the literature, reviewed in the main body of the report plus the results of calculations with the literature data, but it also includes other data on mechanical and heat transfer properties, thermal shock resistance, crystal structure, electrical and magnetic properties, availability, and cost.

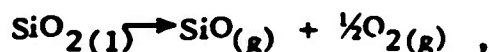
#### A. DECOMPOSITION REACTIONS AND HEAT OF VAPORIZATION

The two processes below have been considered but under equilibrium conditions (Eq. 1) decomposition to form SiO and O<sub>2</sub> has been shown to be the most important reaction.



#### B. VAPOR PRESSURE

The vapor pressure of SiO<sub>2</sub> is not a unique function of temperature but is also very sensitive to the presence of oxidizing or reducing agents in the atmosphere. The total vapor pressure (p<sub>t</sub>) versus temperature (T) for silica under neutral conditions, where the decomposition is essentially



is

$$p_t = 3/2 e^{18.41 \left(1 - \frac{3160}{T}\right)} = 3/2 e^{18.41(1 - 5680/T_R)} ,$$

where

$$P_t = P_{SiO} + P_{O_2} ,$$

$$P_{SiO} = 2/3 P_t ,$$

$$P_{O_2} = 1/3 P_t ,$$

$P_t$ ,  $P_{SiO}$ , and  $P_{O_2}$  are in atmospheres,

$$T = ^\circ\text{Kelvin } (^{\circ}\text{K})$$

$$T_R = ^\circ\text{Rankine } (^{\circ}\text{R})$$

This formula is estimated to be accurate to  $\pm 50$  percent near  $3,000^{\circ}\text{K}$  and applies to the temperature range above  $2,000^{\circ}\text{K}$ . It predicts a total vapor pressure of  $2.17 \times 10^{-3}$  atm. (1.65 mm Hg) at  $2,060^{\circ}\text{C}$  ( $2,330^{\circ}\text{K}$ ). This is much lower than the value of 11 mm reported at this temperature by Ruff et al.<sup>5</sup> However, their measurement was performed only once and they stated that reducing conditions made their vapor pressure determination give high values. For approximate estimates of  $P_{SiO}$  under neutral conditions see Fig. 4.

Small contributions to the vapor pressure are made by other equilibrium products. (See Fig. 11). The following is a typical expected neutral equilibrium mixture at a temperature of  $3,000^{\circ}\text{K}$  ( $2,727^{\circ}\text{C}$ ,  $4,940^{\circ}\text{F}$ ,  $5,400^{\circ}\text{R}$ ):

<u>Species</u>	<u>Partial Pressure (atm.)</u>
SiO	0.43
O <sub>2</sub>	0.18
O	0.05
SiO <sub>2</sub>	0.04
Si <sub>2</sub> O <sub>2</sub>	$5 \times 10^{-5}$
Si	$1.3 \times 10^{-6}$
$P_t$	= 0.70 atm

For the effects of an oxidizing atmosphere under different total pressures, see Figures 13-16.

### C. MOLECULAR WEIGHT

The molecular weight is 60.06.

### D. MELTING POINT

Fused silica, being a supercooled liquid, has no recognized melting point. It softens (viscosity  $\approx 10^{7.6}$  poises) at  $1,500^\circ\text{C}$ <sup>52</sup>. The various crystalline forms of  $\text{SiO}_2$  do melt, however.

<u>Form</u>	<u>Melting point</u>	
	<u><math>^\circ\text{F}</math></u>	<u><math>^\circ\text{C}</math></u>
cristobalite	3,140	1,728
tridymite	3,056	1,680
quartz	2,930	1,610

### E. BOILING POINT

As indicated in (A) and (B) of this appendix, vaporization of  $\text{SiO}_2$  yields predominantly a mixture of  $\text{SiO}$  and  $\text{O}_2$ . Lesser amounts of  $\text{SiO}_2$  gas and  $\text{O}$  atoms are formed. The calculated normal boiling point (vapor pressure = 1 atm) is  $5,072^\circ\text{F}$  ( $2,800^\circ\text{C}$ ,  $3,070^\circ\text{K}$ ).

### F. VISCOSITY

A viscosity relation which is valid for the temperature range of  $2,197^\circ\text{K}$  to  $2,333^\circ\text{K}$  ( $1,924^\circ\text{C}$  to  $2,060^\circ\text{C}$ ) is

$$\log_{10}\eta = 28,200/T(^{\circ}\text{K}) - 7.73 \quad 53, 54$$

### G. SPECIFIC HEAT

For vitreous or fused silica the molar heat capacity relation given by Kelley<sup>13</sup> covers the range of  $298^\circ\text{K}$  to  $2,000^\circ\text{K}$ . Its accuracy is  $\pm 2$  percent.

$$C_p = 13.38 + 3.68 \times 10^{-3}T - 3.45 \times 10^{-5}T^2 - 2$$

where

$C_p$  = calorie/mole - degree K

$T$  = °Kelvin

## H. SENSIBLE HEAT PLUS HEAT OF VAPORIZATION

The sensible heat required to bring fused silica from 298° K to 3,000° K is found to be 1,524 Btu/lb (or 50,670 calorie/mole). Going from 298° K to 3,070° K requires 1,570 Btu/lb (or 52,190 calorie/mole). Assuming that the heat of vaporization at 3,070° K does not differ appreciably from that at 3,000° K, one can obtain the following total heat absorptions for the principal decomposition equations (A-1) and (A-2) of this appendix.

<u>Temperature</u>	<u>Process</u>	<u>Btu/lb</u>	<u>Calorie/mole</u>
3,000° K	Reaction (1)	6,650	222,183
3,000	(2)	5,336	177,877
3,070	(1)	6,700	
3,070	(2)	5,386	
3,070 (for normal equilibrium mixture:	0.915 moles SiO by (1)	6,790	
	0.11 moles O by 1/2 O <sub>2</sub> → O		
	0.085 moles SiO <sub>2</sub> by (2)		

These data show that the total heat of decomposition is essentially controlled by reaction (1).

That is even when the equilibrium mixture at 3,070° K is considered the extra energy required to dissociate O<sub>2</sub> is partially offset by the reduced heat required to evaporate gaseous SiO<sub>2</sub>. It can also be seen that the uncertainty in the heat of reaction (1) at 3,000° K was of the order of 5,000 calorie/mole or 150 Btu/lb. Thus, for most purposes, it is sufficient to use only the data from reaction (1).

## I. DENSITY

The density of pure fused silica is 137.3 lb/ft<sup>3</sup> or 2.20 gm/cm<sup>3</sup>.<sup>52</sup>

## J. THERMAL CONDUCTIVITY

At 0° C, fused silica has a thermal conductivity of 0.795 Btu/hr ft° F or 33 x 10<sup>-4</sup> calorie - cm/sec - cm<sup>2</sup> - °C.<sup>55</sup>



## K. COEFFICIENT OF THERMAL EXPANSION

The coefficient of thermal expansion for clear, fused silica from 20° - 320° C is reported to be  $3.05 \times 10^{-7}/^{\circ}\text{F}$  or  $0.55 \times 10^{-6}/^{\circ}\text{C}$  by G. E.<sup>55</sup>, and from 0° - 300° C it is reported to be  $3.1 \times 10^{-7}/^{\circ}\text{F}$  or  $0.56 \times 10^{-6}/^{\circ}\text{C}$  by Corning.<sup>52</sup>

## L. YOUNG'S MODULUS

Clear, fused silica, at room-temperature is reported to have a Young's Modulus of  $10.1 \times 10^6 \text{ lb/in}^2$  or  $7,138 \text{ kg/mm}^2$  by G. E.<sup>55</sup>

## M. TENSILE STRENGTH

In 1/4 inch rods, fused silica has a strength of  $7,100 \text{ lb/in}^2$  or  $5 \text{ kg/mm}^2$ ; whereas in fibres, it has a strength of 43,500 to 116,000  $\text{lb/in}^2$  or 30.6 -  $81.6 \text{ kg/mm}^2$ .<sup>55</sup>

## N. THERMAL SHOCK RESISTANCE

Fused silica has excellent thermal shock resistance.<sup>11</sup>

Other forms of silica have poor resistance at certain temperatures because of volume changes which occur at inversion points.

A 6 x 6 x 1/4-inch annealed plate of fused silica can withstand a 1,000° C<sup>52</sup> differential from being plunged into cold water after oven heating.

## O. HARDNESS

The hardness of fused silica is 4.9 on the Mohs Scale<sup>55</sup> whereas cristobalite, quartz, tridymite have a value of 7.0 on the Mohs Scale.<sup>45</sup>

## P. CRYSTALLINE STRUCTURE

Pure  $\text{SiO}_2$  is a polymorphic material. The vitreous or glassy form of  $\text{SiO}_2$  is a metastable, undercooled liquid at all temperatures below 1,728° C (2,000° K). The rate of transformation of vitreous  $\text{SiO}_2$  into the other forms may become measurable above 1,000° C. Impurities also affect the rate of transformation. Listed below are the stability ranges for the various forms of  $\text{SiO}_2$ :

<u>Form</u>	<u>Temperature range of stability</u>
Silica glass	$T > 1,728^{\circ} \text{C}$
$\beta$ - Cristobalite	$1,728^{\circ} - 1,470^{\circ} \text{C}^{12}$
$\beta$ - Tridymite	$1,470^{\circ} - 870^{\circ} \text{C}^{11}$
$\beta$ - Quartz	$870^{\circ} - 573^{\circ} \text{C}$
$\alpha$ - Quartz	$573^{\circ} -$

In fused silica glass, the Warren model is generally accepted<sup>56</sup> to represent the short range order. Being a liquid-like material<sup>57</sup> there is no long-range order greater than about 4 or 5 interatomic distances. According to the Warren view each silicon atom is surrounded tetrahedrally by four oxygen atoms. Each oxygen atom is shared by two silicon atoms. The SiO distance is about 1.6 Å, the O-O distance is 2.65 Å, and the Si-Si distance is 3.2 Å.

#### Q. ELECTRICAL RESISTIVITY<sup>11</sup>

The electrical resistivities of various forms of silica are:

<u>Form</u>	<u>Temperature</u>	<u>Resistivity</u> <u>(ohm-cm)</u>
Vitreous	$20^{\circ} \text{C}$	$1 \times 10^{15}$
	$600^{\circ} \text{C}$	$7 \times 10^6$
	$1,300^{\circ} \text{C}$	$4 \times 10^5$
Crystalline (quartz)	$20^{\circ} \text{C}$	$1 \times 10^{14}$
	$1,300^{\circ} \text{C}$	$5 \times 10^3$
	$20^{\circ} \text{C}$	$2 \times 10^{16}$
	$1,300^{\circ} \text{C}$	$1 \times 10^4$
		to prin- cipal axis
		⊥ to prin- cipal axis

#### R. DIELECTRIC CONSTANT<sup>11</sup>

The dielectric constants of silica are:

<u>Form</u>	<u>Temperature</u>	<u>Dielectric Constant</u>
Vitreous	20° C	3.75
Crystalline (quartz)	20° C	4.6    to direction of field
		4.5 ⊥ to direction of field

## S. MAGNETIC SUSCEPTIBILITY<sup>11</sup>

The magnetic susceptibilities of silica are:

<u>Form</u>	<u>Susceptibility</u>
Vitreous	$-0.45 \times 10^{-6}$ magnetic units/gm
Crystalline (quartz)	$-0.45 \times 10^{-6}$ magnetic units/gm

## T. PURITY

Fused silica can be obtained as one of the purest chemicals known. For example, Corning's commercial grade is 99.9 percent pure. It is possible to obtain a grade of 99.99 percent purity for use in delay lines, and a grade of 99.999 percent purity is available for use in spectroscopy. The cost climbs rapidly with purity.

Some analyses for the Corning grades are presented below. It should be emphasized that the impurities given need not be unavoidable since precautions can be taken to remove certain impurities if necessary. The type 7943 grade (99.99 percent purity) is a desirable optical grade for infrared work because of the absence of the OH group. As of March 1958 it was not available in sizes over 1/8-inch thick. Type 7940 can be obtained in flat sheets to 20 inches in diameter and up to 3 inches thick.<sup>58</sup>

<u>Impurity</u>	<u>Type 7940 (percent)</u>	<u>Type 7943 (percent)</u>
OH	0.1	0.00
Li	< 0.0001	
Na	0.00003	0.001

<u>Impurity</u>	<u>Type 7940 (percent)</u>	<u>Type 7943 (percent)</u>
K	0.0001	0.0003
Fe	0.002	0.001
Cu	0.00001	0.00001
Ti	0.0005	0.0005
Bi		0.0000047
P		0.000010
As		0.00000057
Sb		0.00000051
Zr, V, Pb, Sn, Ge, Mo, Ca		not detected, and less than ~ 10 ppm = 0.001 percent
Al <sub>2</sub> O <sub>3</sub>	0.001	59

A typical analysis of some G. E. fused silica is presented below. The source is a Brazilian quartz sand. The data were given to D. Walker by K. Field of General Electric. <sup>60</sup>

<u>Impurity</u>	<u>Percent</u>
Fe <sub>2</sub> O <sub>3</sub>	0.0017
Al <sub>2</sub> O <sub>3</sub>	0.014
TiO <sub>2</sub>	nil
ZrO <sub>2</sub>	nil
K	0.0003
CaO	< 0.0003
MgO	< 0.0007
C	none
B	< 0.0001

## U. AVAILABILITY

Fused or vitreous silica is produced by at least three manufacturers in this country:

- a. Corning Glass Works, Corning, New York.
- b. General Electric Company, Lamp Glass Department, Nela Park, Cleveland 12, Ohio.
- c. Amersil Division of Engelhard Industries.

## V. COST

The cost of fused silica is very dependent on the purity, finished form, etc. Some typical prices for G. E. products are shown below:

Form <hr/>	Clear, Fused Quartz <hr/> (Cost/lb.)	Translucent <hr/> (Cost/lb.)
rod, 1/16-inch diameter	\$50.00	--
rod, 3/16-inch diameter	30.00	\$12.00
ingot, to 18 1/2 inches diameter	15.00	--

**APPENDIX B**  
**ILLUSTRATIONS**

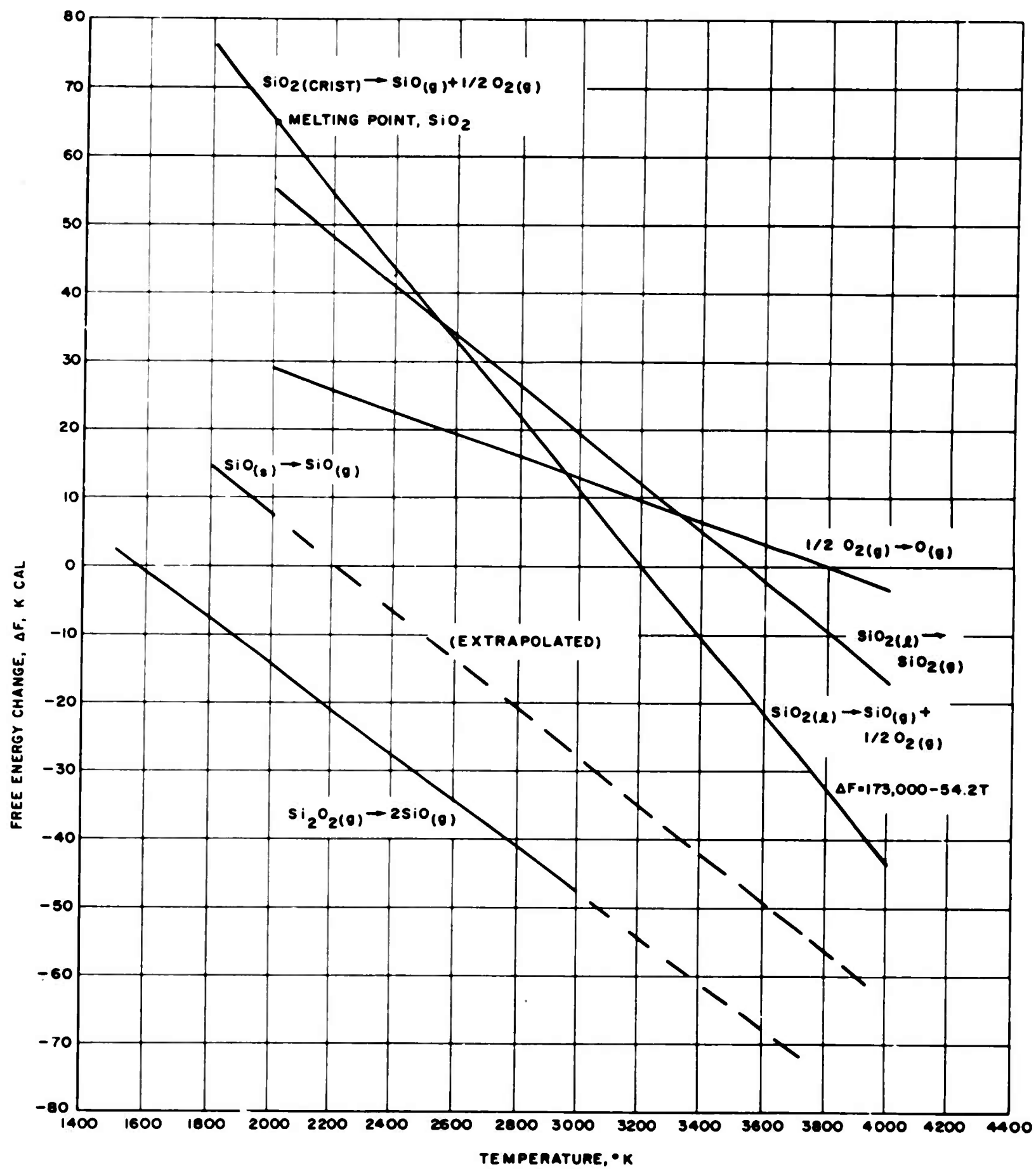


Figure 1 FREE ENERGY CHANGES OF REACTIONS IN  $\text{SiO}_2$  DECOMPOSITION  
VERSUS TEMPERATURE  
 4508

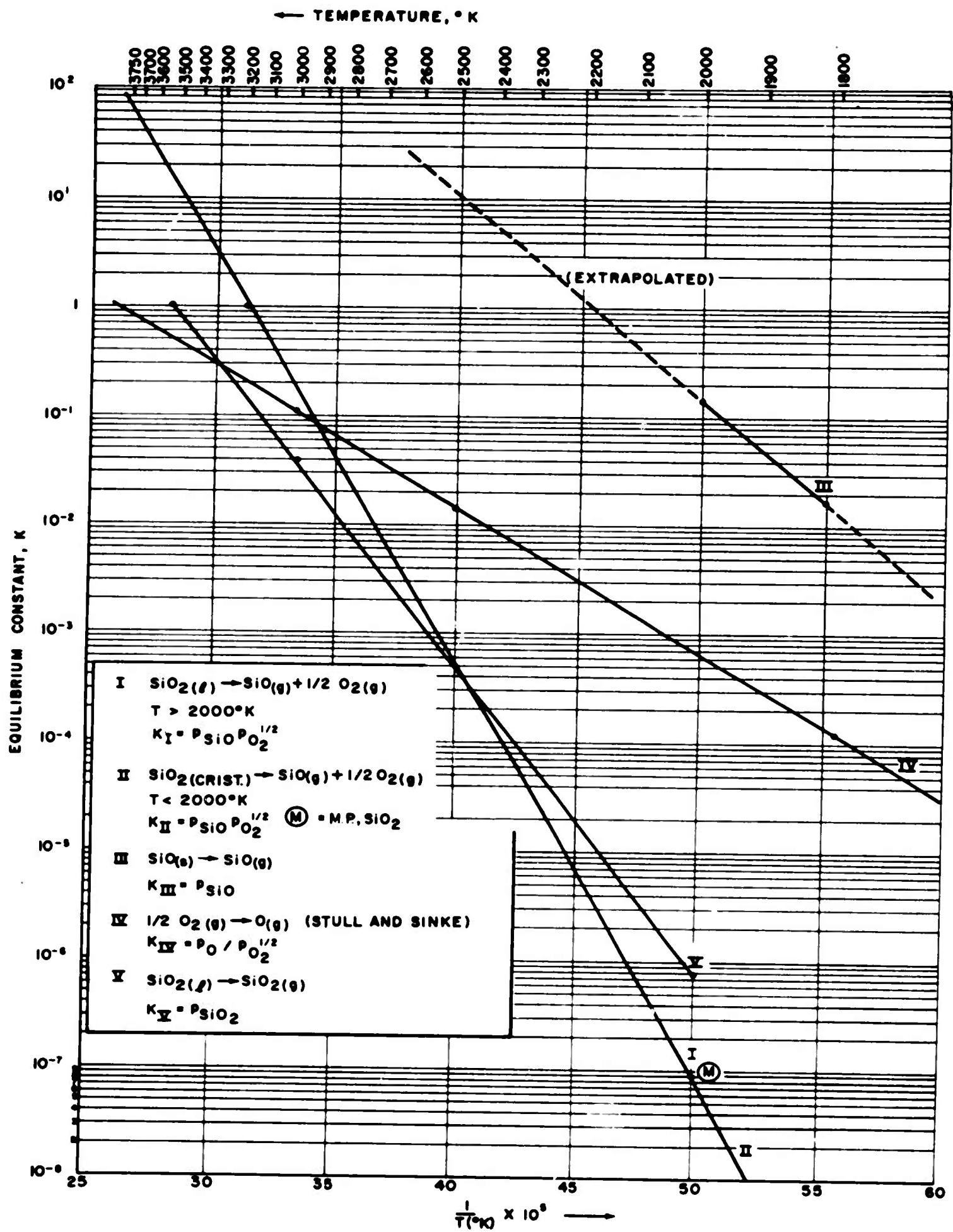


Figure 2 EQUILIBRIUM CONSTANTS OF  $\text{SiO}_2$  DECOMPOSITION REACTIONS  
 VERSUS  $\frac{1}{T}$   
 4509



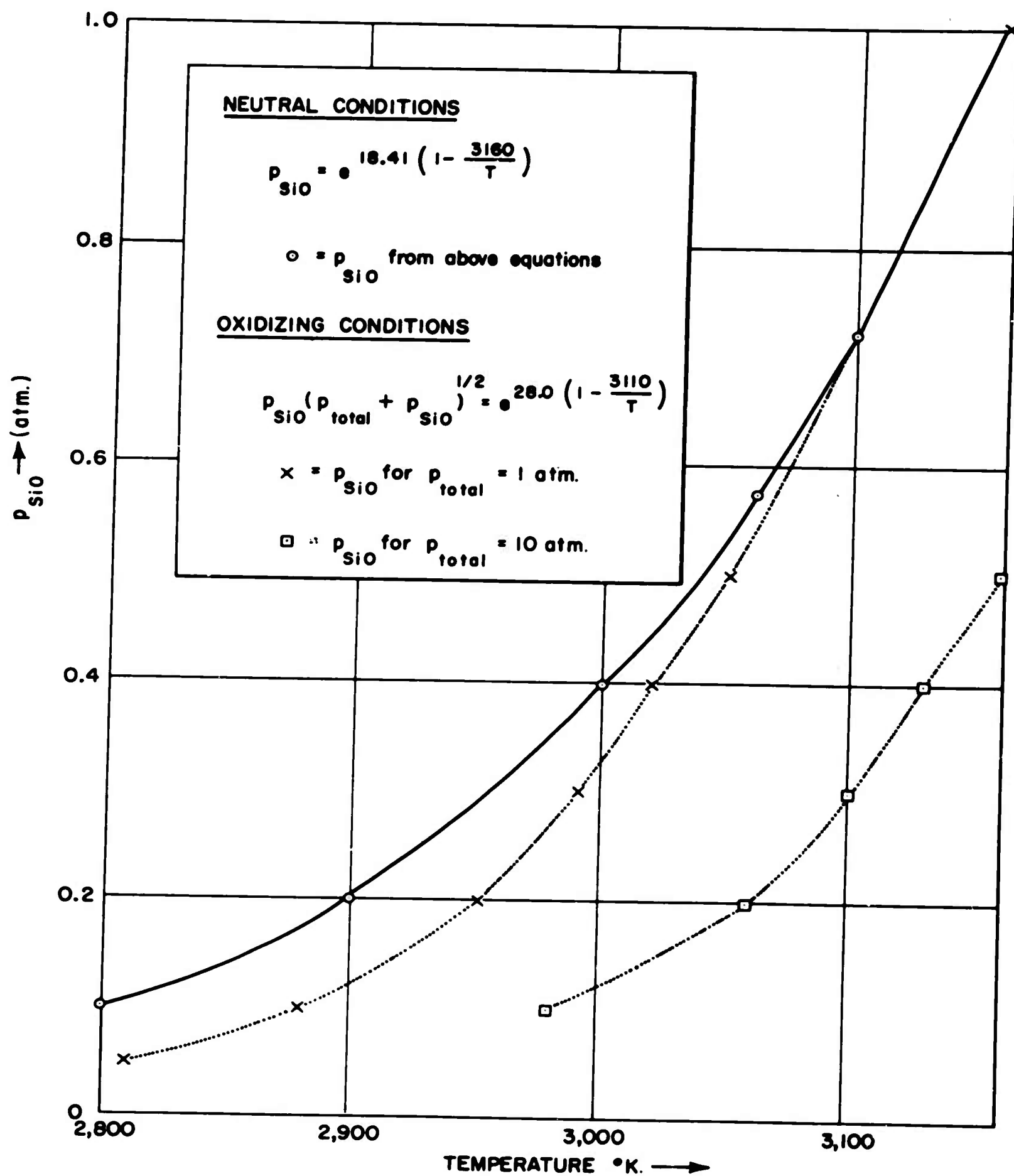


Figure 3 PARTIAL PRESSURE OF  $\text{SiO}_{(\text{g})}$  OVER  $\text{SiO}_2$  VERSUS TEMPERATURE  
NEGLECTING  $\text{O}_2$  DISSOCIATION  
4510

S

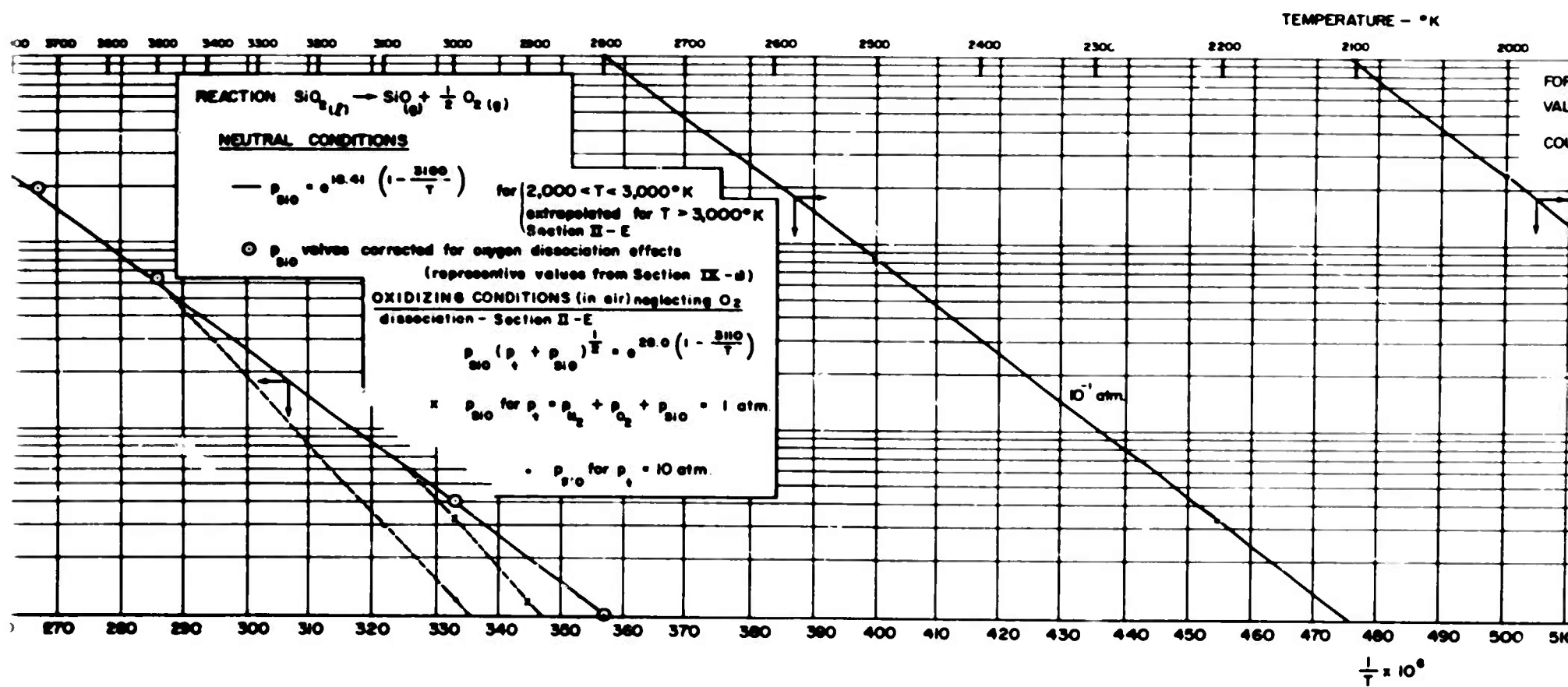
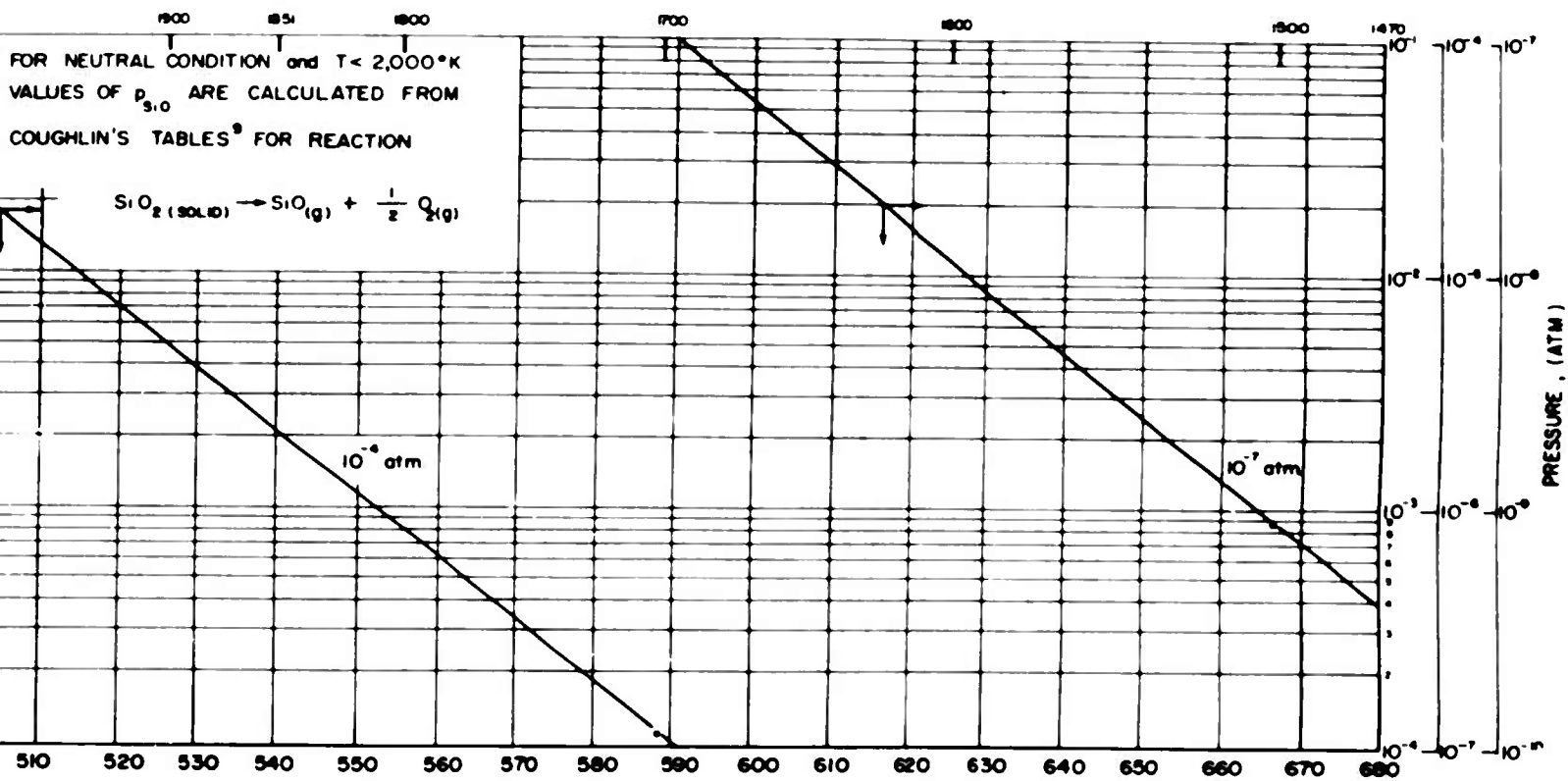


Figure 4 PARTIAL PRESSURE OF  $\text{SiO}(\text{g})$  OVER  $\text{SiO}_2(\text{s})$  VS  
 TEMPERATURE NEGLECTING  $\text{O}_2$  DISSO



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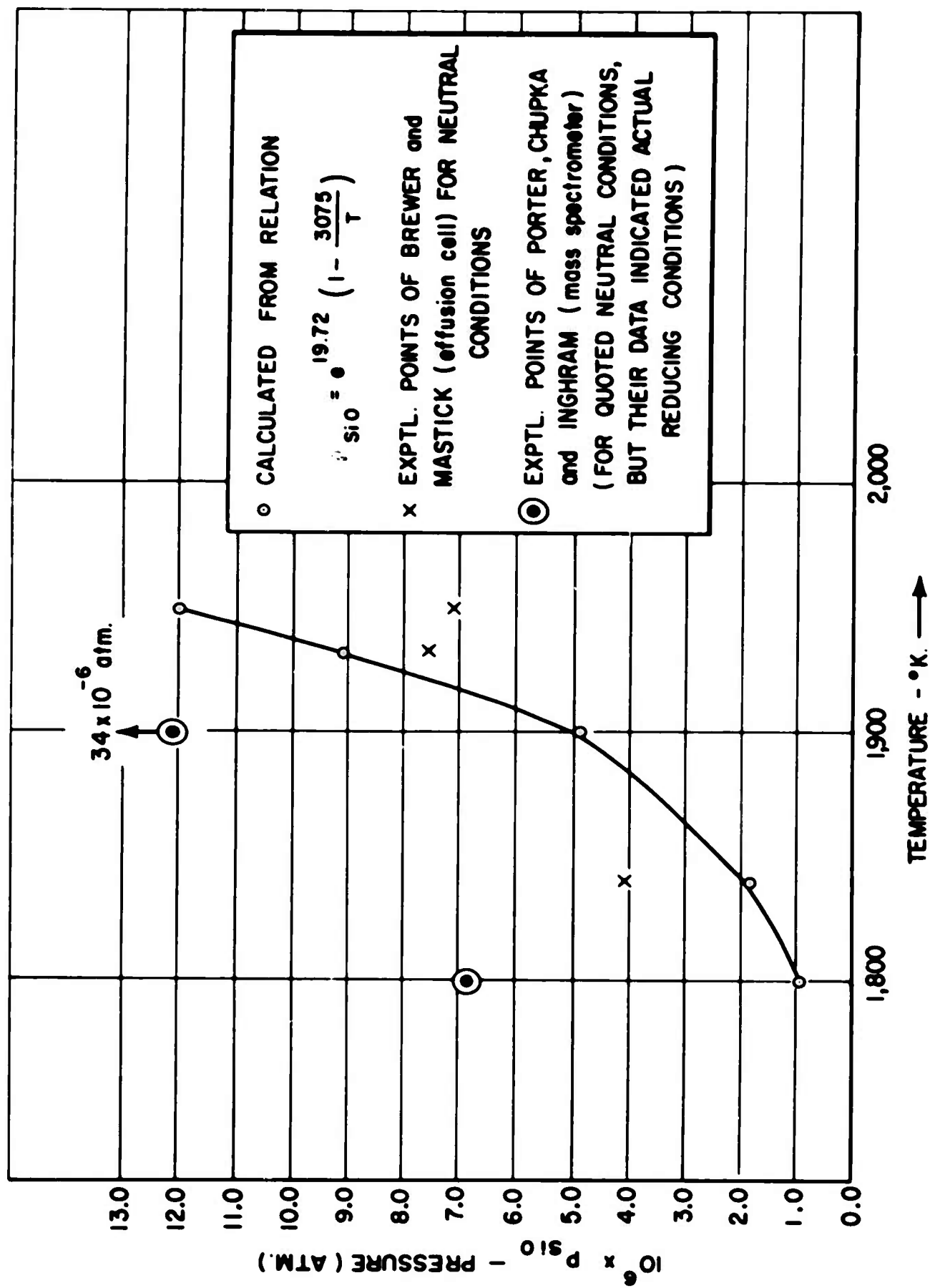


Figure 5 PARTIAL PRESSURE OF  $SiO(g)$  OVER CRISTOBALITE VERSUS TEMPERATURE FROM 1,800° TO 2,000°K

4512

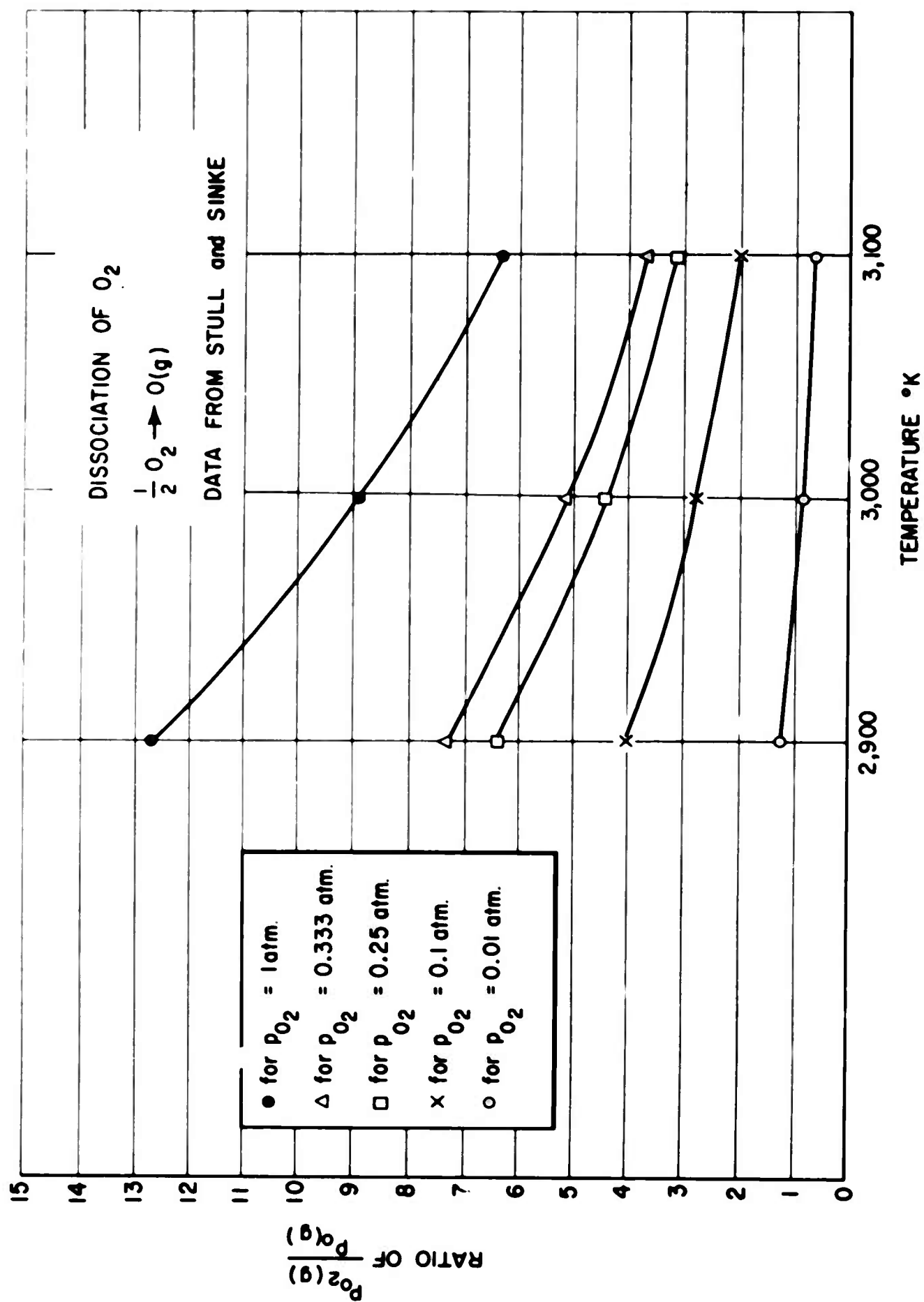


Figure 7 DISSOCIATION PRESSURE RATIOS OF OXYGEN VERSUS TEMPERATURE  
NEAR 3,000°K  
4514

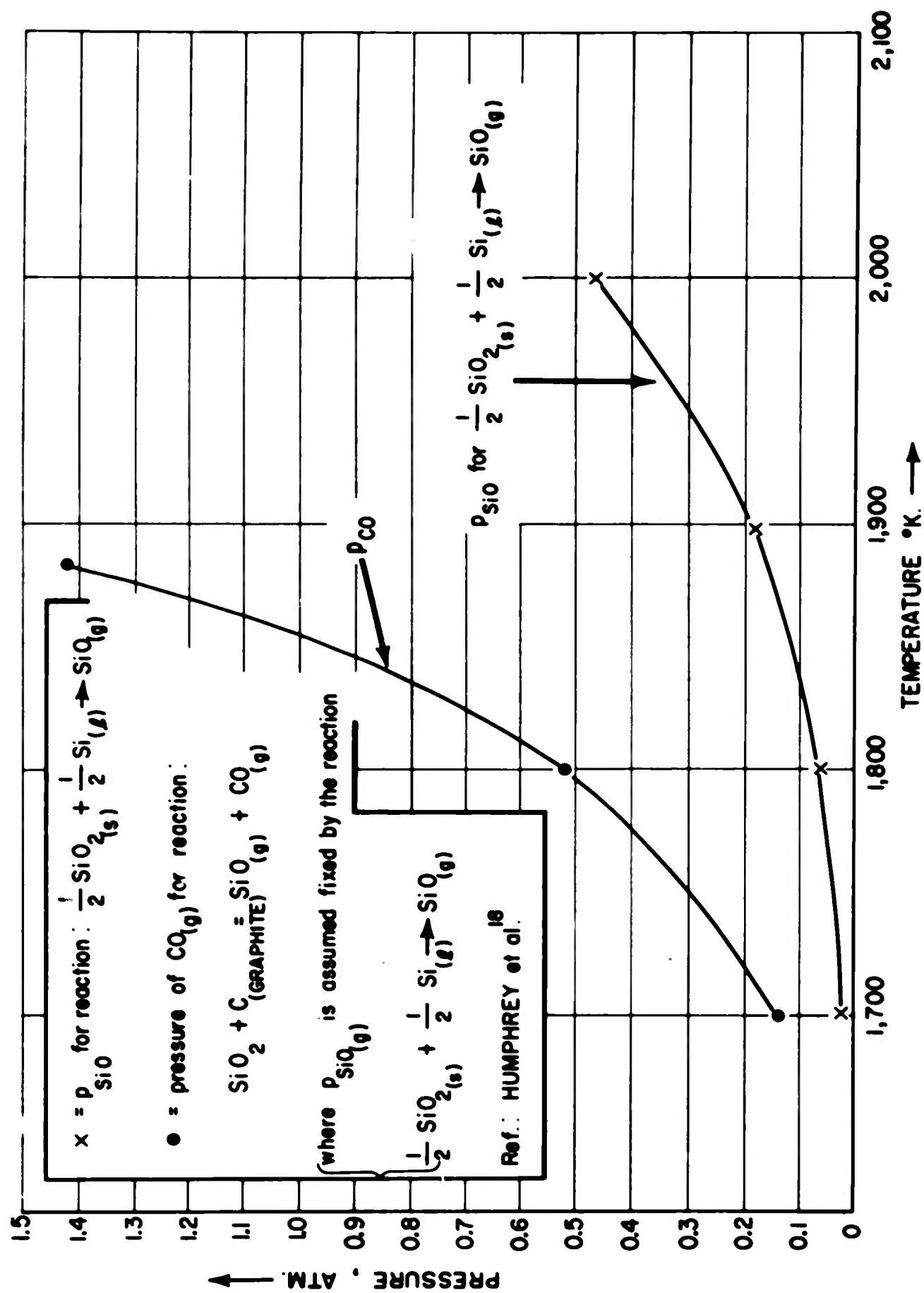


Figure 9 PARTIAL PRESSURES OF IMPORTANT SPECIES WHEN  $\text{SiO}_2$  IS DECOMPOSED BY CARBON OR SILICON

4516

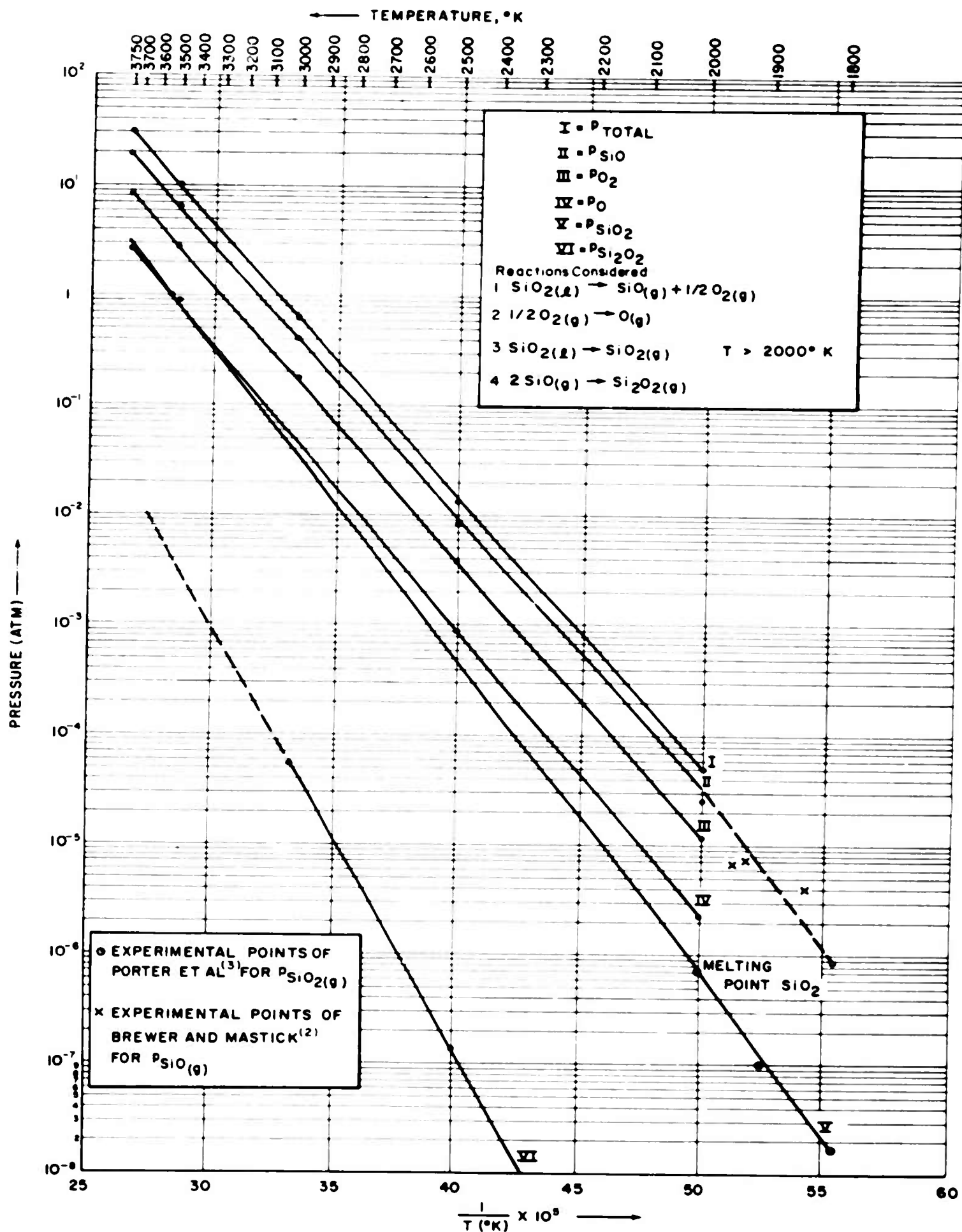


Figure 11 PARTIAL PRESSURES OF PRODUCTS WHEN  $\text{SiO}_2$  DECOMPOSES IN AIR VERSUS  $\frac{1}{T}$  UNDER NEUTRAL CONDITIONS AND INCLUDING OXYGEN DISSOCIATION

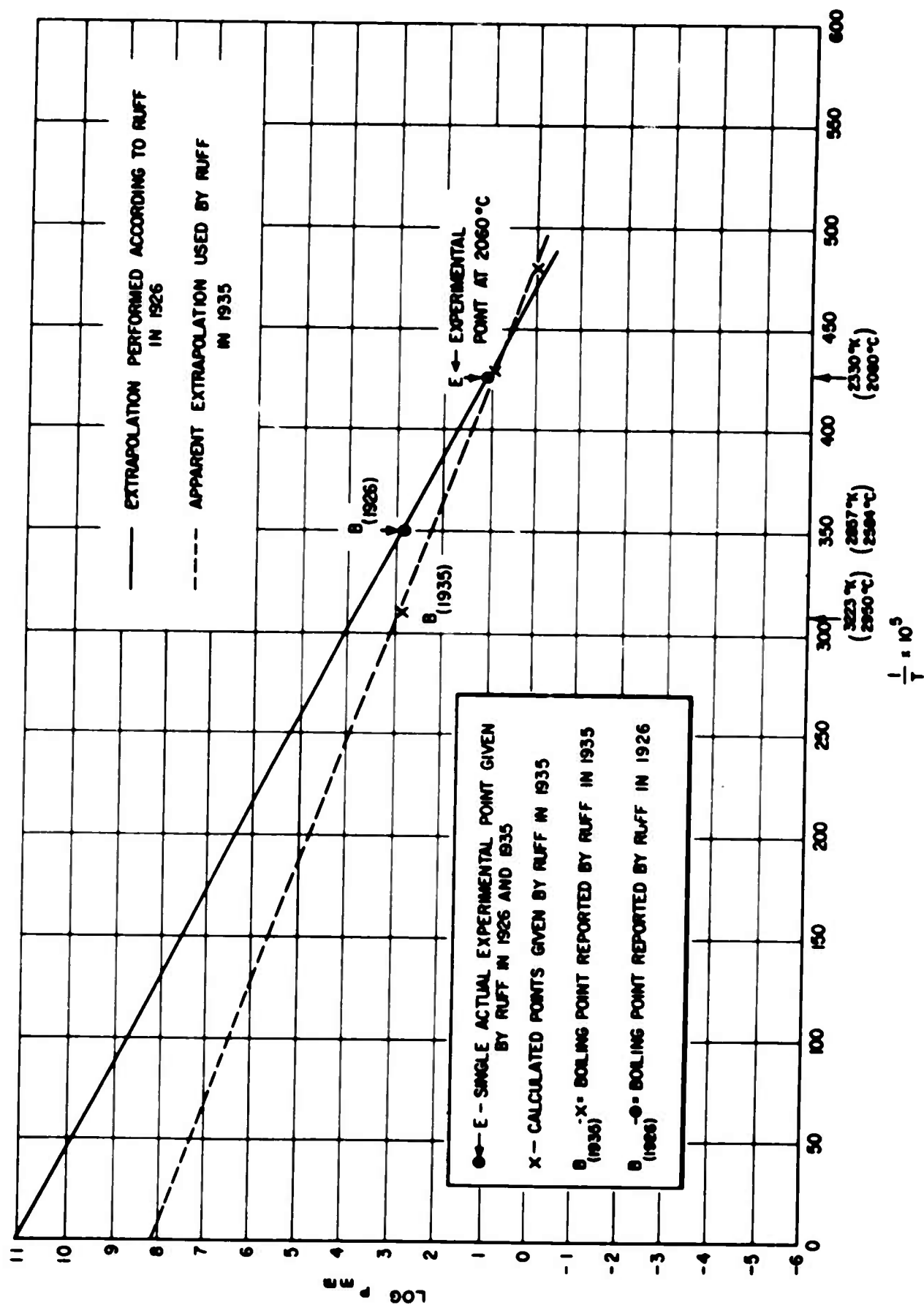


Figure 12 REPEAT OF RUFF'S EXTRAPOLATION FOR THE  $\text{SiO}_2$  BOILING POINT  
4519



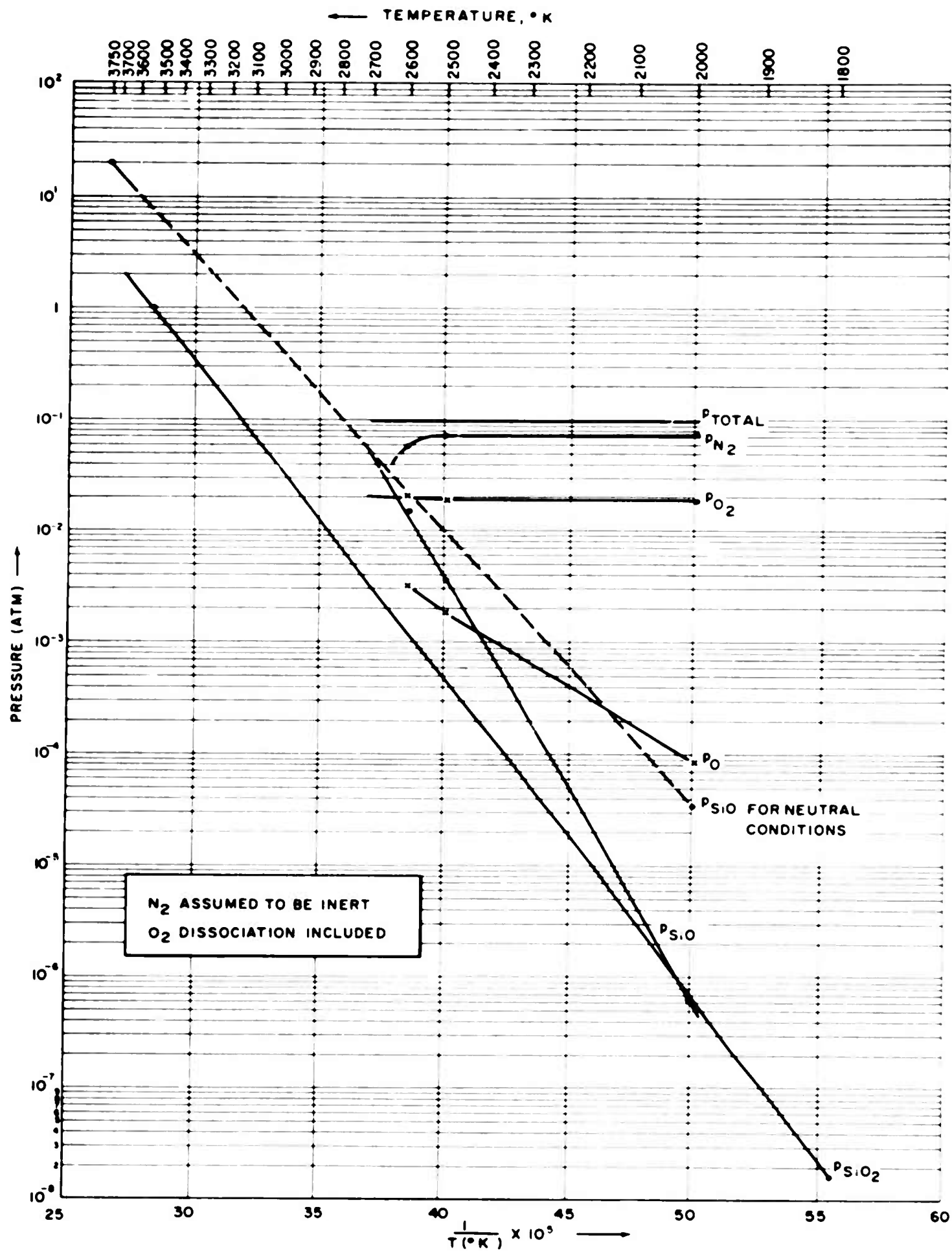


Figure 13 PARTIAL PRESSURES OF PRODUCTS WHEN  $\text{SiO}_2$  DECOMPOSES IN AIR AT 0.1 ATM VERSUS  $\frac{1}{T}$

4520

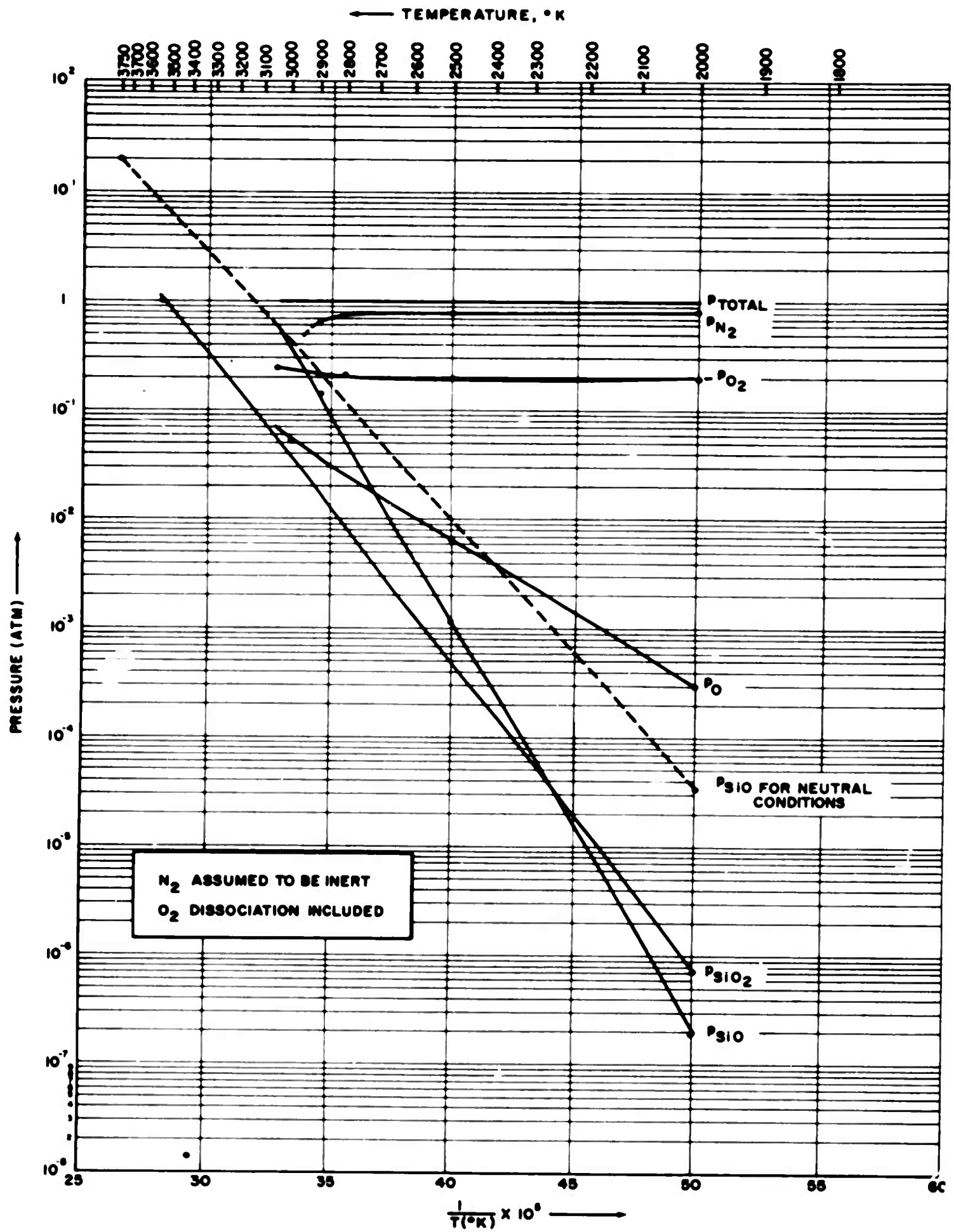


Figure 14 PARTIAL PRESSURES OF PRODUCTS WHEN SiO<sub>2</sub> DECOMPOSES IN AIR AT 1.0 ATM VERSUS  $\frac{1}{T}$

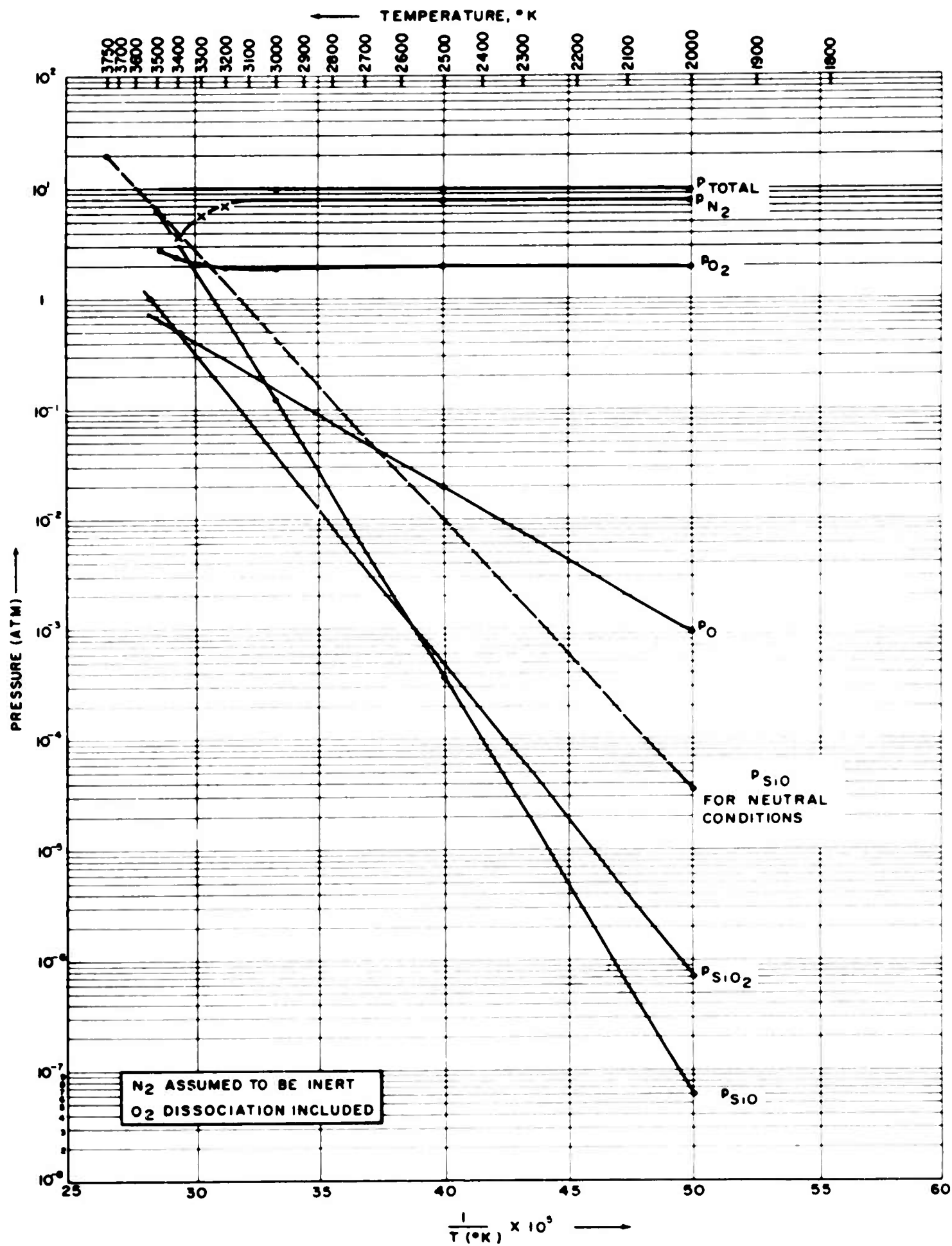


Figure 15 PARTIAL PRESSURES OF PRODUCTS WHEN  $\text{SiO}_2$  DECOMPOSES IN AIR AT 10 ATM VERSUS  $\frac{1}{T}$

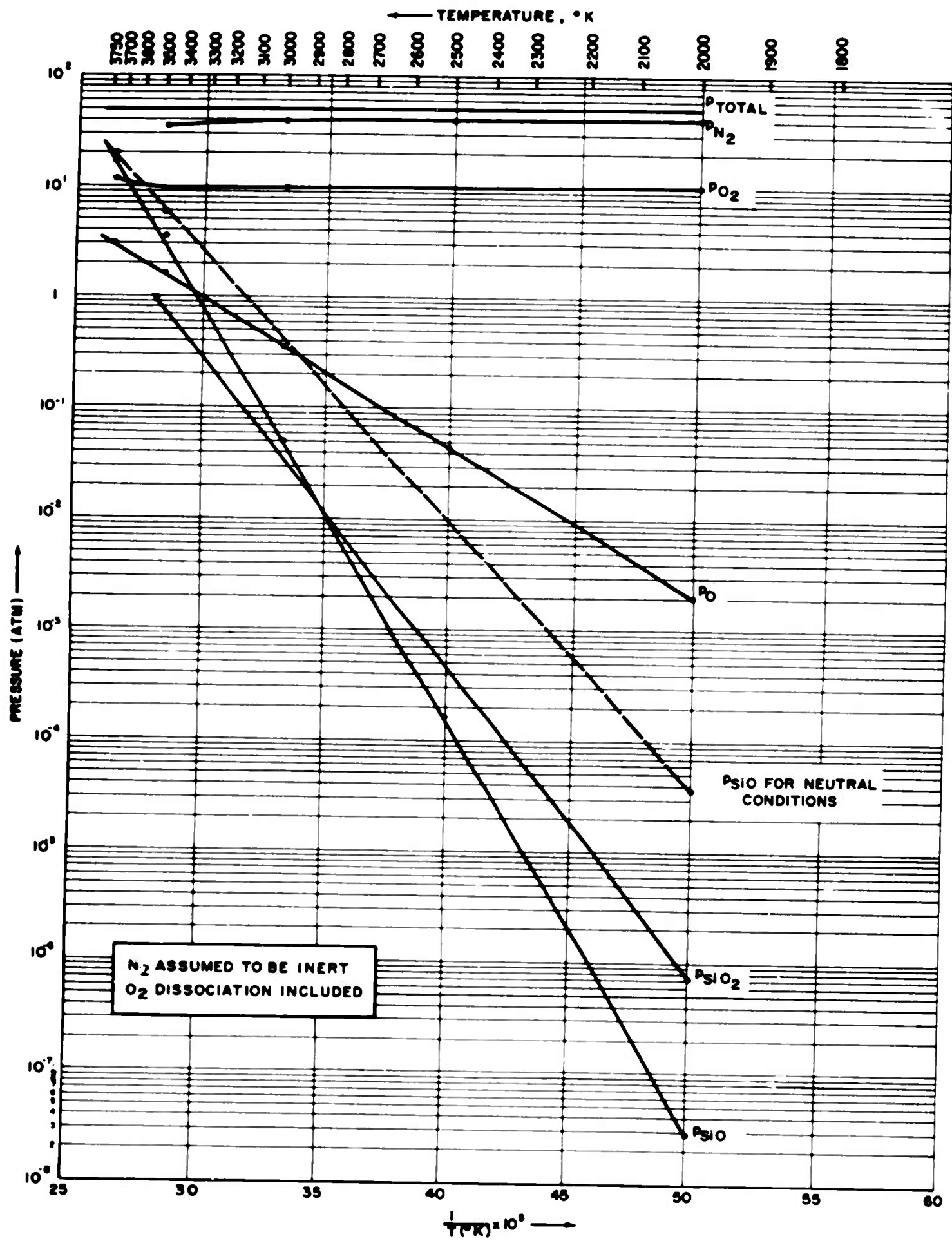


Figure 16 PARTIAL PRESSURES OF PRODUCTS WHEN SiO<sub>2</sub> DECOMPOSES IN AIR AT 50 ATM VERSUS  $\frac{1}{T}$

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